Thermo and Photo-Electret State in Iodine Doped Polystyrene films

Thesis submitted For the Degree

of

DOCTOR OF PHILOSOPHY

in

Physics

by

Manoj Kumar Tiwari

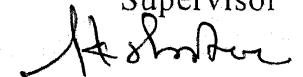Lecturer in Physics "Adhock"

M.P. College, Konch

to

BUNDELKHAND UNIVERSITY JHANSI

D.V. College Orai

2002

CERTIFICATE

It is certified that *Manoj Kumar Tiwari*
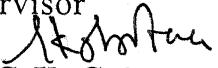
worked for more than three years under my guidance.

Supervisor

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DECLARATION

I here by declare that with the exception of the guidance received from my guide, this thesis is my own unaided work.

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PREFACE

One of the important problems of present day electrical engineering is the production of low cost materials possessing fixed electrical and optical characteristics to be used in modern solid state devices. Electrical properties of polymeric matrices can be greatly influenced by impurities present in them. Doping of polymers with suitable additives can be utilized to produce such materials. With this view, polystyrene was doped with iodine and the electrical and optical properties of doped films were investigated.

The thesis has been divided in seven different chapters.

Chapter-1 " Introduction" surveys briefly the concerned literature and introduces the problem. Chapter -2 "Experimental details" describes film preparation, thickness measurement, doping procedure, electrode assembly and measuring instruments. Chapter-3" Electrical conduction" reports transient behaviour of current and steady state current-voltage characteristics as a function of electrode material, film thickness and iodine concentration. It also reports temperature dependence

of current at fixed voltage. Chapter-4 "Dielectric properties" investigates frequency and temperature, frequency and iodine concentration.Chapter-5 "Photodepolarization current" describes current decay mode by varying the polarizing time, polarizing voltage, electrode material and iodine concentration. Chpater-6 "Thermallly stimulated discharge current" invetigates TSC spectra by varying, polarizing voltage, iodine concentration and electrode material. Chapter -7 "Correlation of different studies" correlates the results of various studies. Summary and references are given at the end.

ACKNOWLEDGEMENT

I owe the deepest sense of gratitude to my supervisor Dr. S.K. Srivastava, Reader in Physics, D.V. College, Orai for his valuable guidance and keen interest during the present investigation. He has been extremely kind and generous in making available to me all the resources at his command.

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I am greatly thankful to the principal D.V. College, Orai for providing facilities to me in conducting this research work.

I am in deep debt to my parents for their blessings and inspiration in completing my work.

Finally, I bow my head before the supreme authority of God who enlightened my path and strengthened me internally to face all odds in the course of the present investigation.

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SUBJECT	PAGE

Chapter-1

Introduction

INTRODUCTION

A Japanese physicist Equchi (1) invented electret in 1919. Heaviside (2) used the word "electret". After this, the electrets have become the object of numerous experimental and theoretical researches (3-8) and have found an increasingly wider practical applications.

1.1 Electret :

An electret is a piece of a solid which stores quasipermanent electrical charges for extremely long time.

An electret may have real charges, such as surface charge layers or space charges. It may be a true polarization or it may be a combination of these. This is shown schematically. in fig 1.1.1 for a dielectric plate, The true polarization is usually a frozen-in alignment of dipoles. However, real charges comprise of layers of trapped positive and negative charge carriers, often positioned at or near the two surfaces of dielectric, respectively. The electret charges may consist of carriers displaced within molecular domain structures through out the solid, resembling a true dipole polarization. If the charges are displaced to domain boundaries, they are referred to as Maxwell-Wagner polarization.

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Fig 1.1.1 Various charges of an electret

Surface Charge

Space Charges

Dielectric

Dipolar or Displaced Charges

Metal electrode

Compensation charges
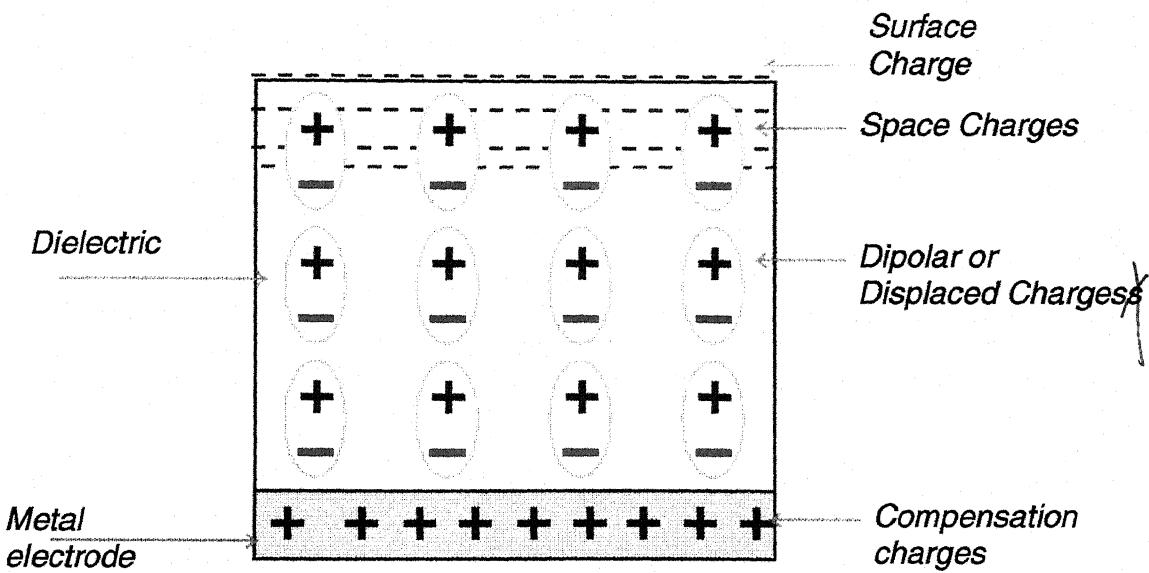
Fig 1.1.2 Schematic cross-section of some typical electrets without electrodes or with grounded electrodes

Nonmetallized monocharge electret

One Sided metallized electret with surface charges and space charges

One Sided metallized electret with surface charges and charges displacedin domains (Maxwell-wanger effect)

Two sided metallized electret with dipolar and space charges
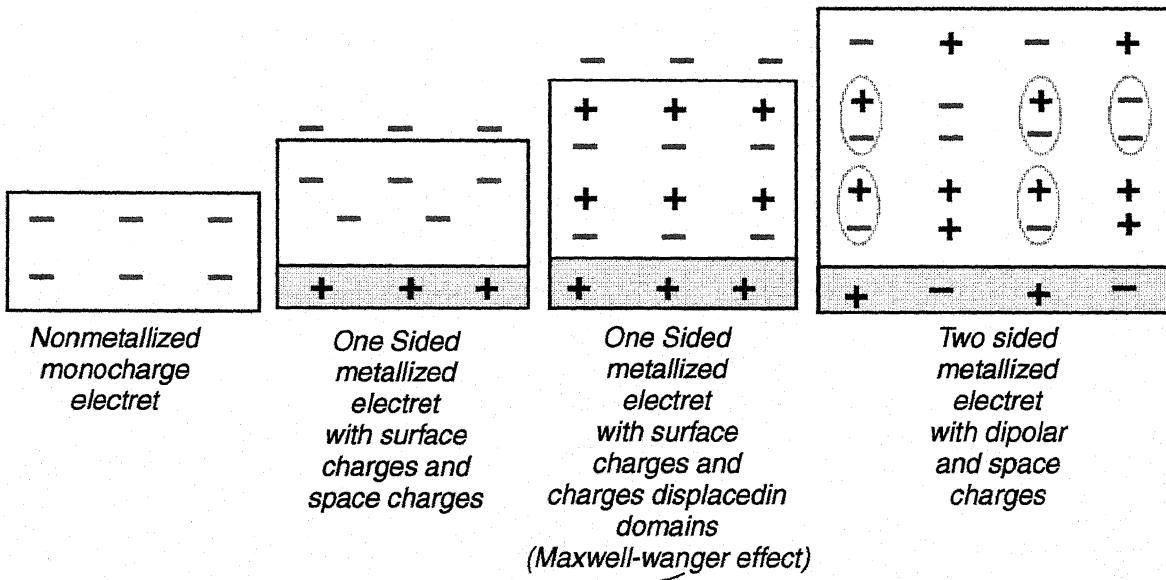
On metallized electrets, a compensation charge may reside on the electrode, unable to cross the energy barrier between metal and dielectric. Examples of various nonmetallized and metallized electrets are shown in fig. 1.1.2.

Mostly the net charge on an electret is zero or close to zero.

Its fields originate due to charge separation, rather than a net charge. An electret not covered by metal electrodes generates an external electrostatic field, It is polarization and real charges do not compensate each other everywhere in the dielectric, such an electret is thus, in a sense, the electrostatic analogue of a magnet. Though, electret properties may be caused by dipolar and monopolar charges but megnetic properties are only due to magnetic dipoles.

1.2   Hetero and homo charges of an electret :-

The intensity of polarizing field appreciably affects the properties of an electret. When the field is small (approximately to 10^4V/Cm), the obtained electret possesses charges opposite to the polarity of the polarizing voltage. If the field is greater than 10^4 V/Cm, the electret receives charges of

Fig 1.2.1 Hetro and homo charges of electret with mechanisms and decay rates

HETEROCHARGE

HOMOCHARGE

ELECTRODE

ELECTRODE

Θ, Θ = injection of homocharges from dielectric-electrode interfaces hetero

$\left(\begin{array}{c}+\\-\end{array}\right)$ = internal hetro charging

⊞ ⊡ = Ion migration

Homo charge

40

20

$\mu c/m^2$ 0

100   200   Time (Mins)

20

Hetro charge

40

Phenomenon of charge reversal

Fig 1.2.1 Hetro and homo charges of electret with mechanisms and decay rates

HETEROCHARGE

HOMOCHARGE

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100   200   Time (Mins)

Phenomenon of charge reversal
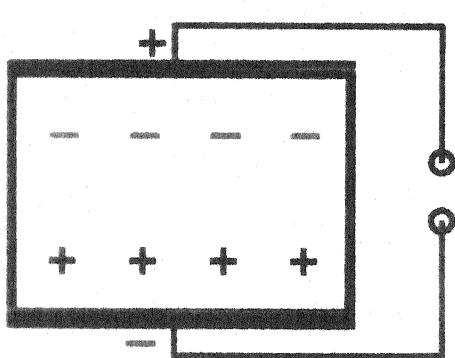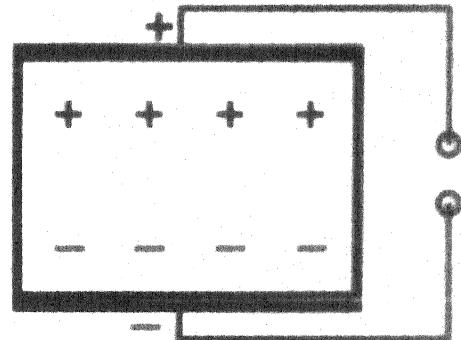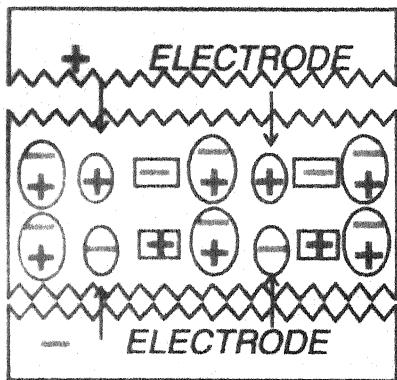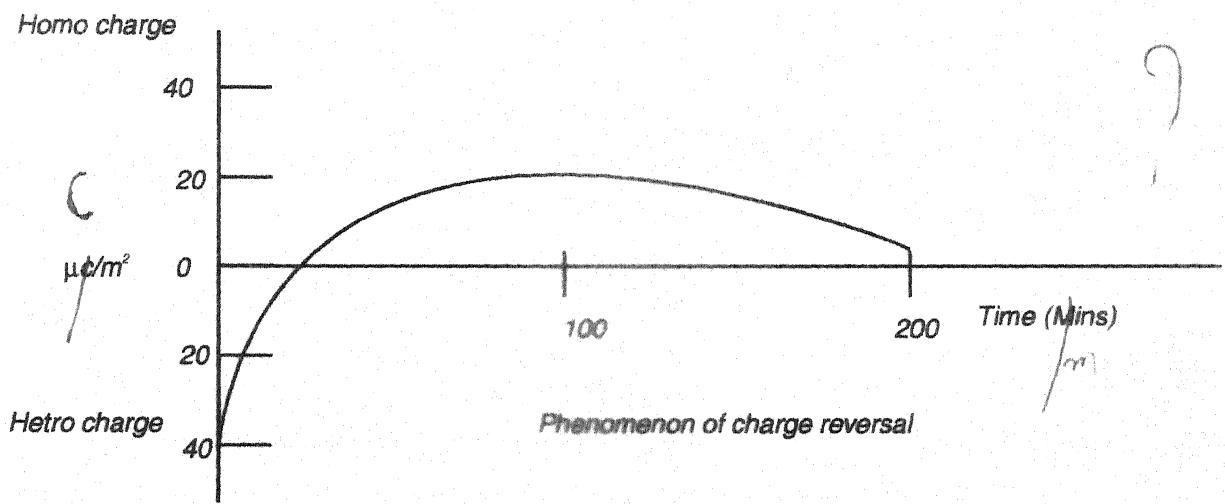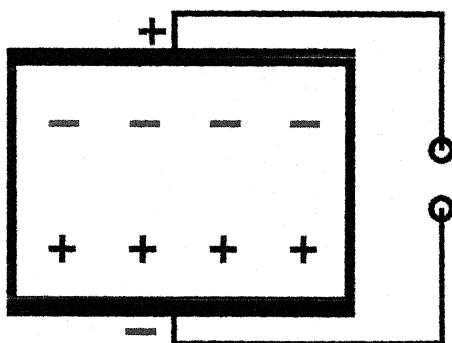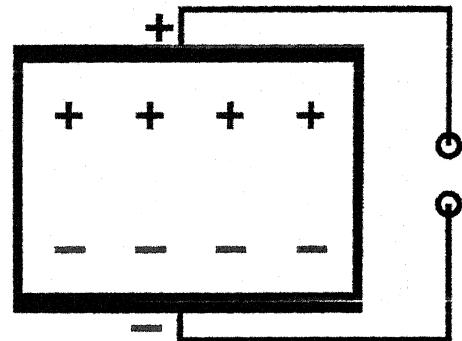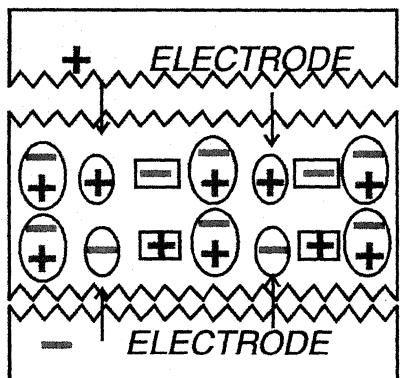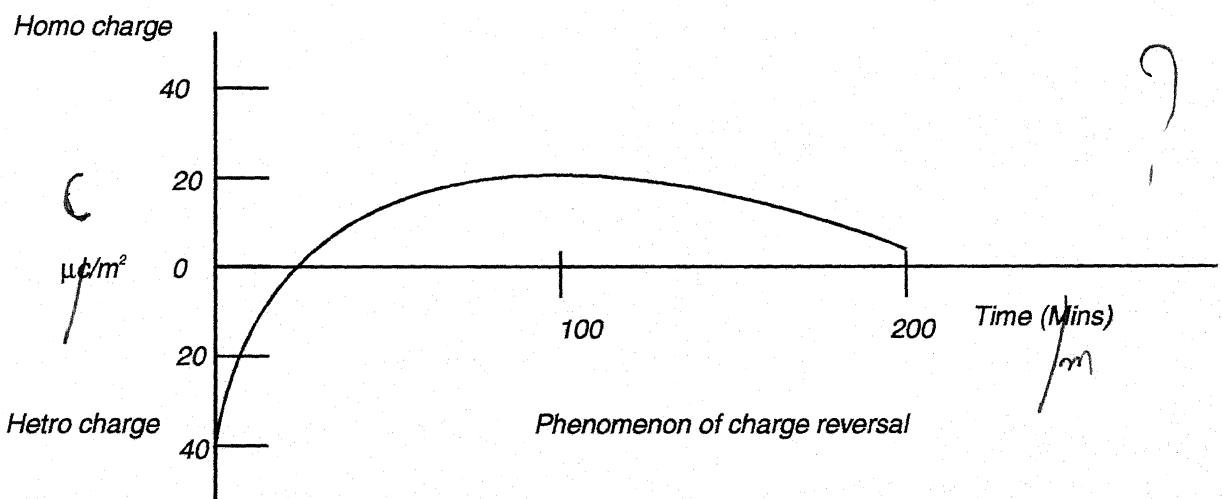
the same sign as the electrodes with which the surfaces of the electret were in contact during polarization. Gemant (9) called the charges of the first type as heterocharges and of the second type as homocharges. Fig. 1.2.1 illustrates two kinds of charges and important mechanisms creating them. Heterocharges are built up by various mechanisms of charge absorption in dielectris. Homocharge is due to the break down at the dielectric-electrode interfaces.

The stability of hetero and homocharges can be different. The decay of heterocharge is more rapid than that of homocharge. This leads to the well-known phenomenon of charge reversal in electrets. These facts are also shown in fig. 1.2.1 Electrets of a large number of dielectrics and polymers exhibit charge reversal. Hetero and homocharge may coxist. If intrinsic homocharge varies slowly with time, charge reversal may not be observed. A lot of investigators (10, 11) have separately observed a homocharge and a heterocharge with the help of, one of the most sensitive technique of thermally stimulated discharge current. It seems that the behavior of two kinds of charges is fundamental and inherent characteristic of the material itself.

Phenomenological theories (12,13) of electret states, based on the two-charge. theory have been proposed verified and confirmed. In the light of huge literature available presently, It may be commented that a single unified theory is still away from reach and more intricate work is required.

1.3   Types of electrets and charging procedures :-

Electrets are subdivided according to physical agencies which produce polarization in a dielectric. When an electric field is applied to a sample, heated to a constant high temperature (preferably near softening point) for some time, and then cooled with the field still on, what is formed, is called a thermoelectret. Photoelectrets are generally made of photoconductive dielectrics. A dielectric placed into a strong field is irradiated with light or ultraviolet light for some time, on switching off the electric field, the specimen becomes a photoelectret. Electroelectrets are obtained under the action of an electric field with out heating a dielectric. Radioelectrets are produced by radioactive radiation in presence of the field. Mechano electrets (14,15) are fabricated by a mechanical effect i.e. deformation or friction of a dielectric. Magnetoelectrets (16)

form when a heated specimen is cted upon by a strong permanent magnetic field with a subsequent cooling in the field: optical magnetoelectret (17) has also been reported. There are other data (not fully confirmed) about other types of electrets. Under an ionizing irradiation, gamma rays, for example, some dielectrics become pseudo electrets, obtained without the voltage.

A variety of techniques (18-21) for the charging of insulators has been described in the literature. Foremost among them are thermal methods using simultaneous application of heat and electric field, corona and Tounsend discharge methods and electron bombardment methods using penetrating beams as well as nonpenetrating beams.

1.4   A note on history of electret research :-

Gray (22) in 1732 mentioned attractive power of waxes, rosins and sulphur. Nearly a century later, in 1839, Faraday (23) theorized about electrical properties of materials. The existence of electret was surmised by the Russian academician Epinus, and later by the English physicist Heaviside (2) who introduced in 1896 the term "electret" and studied some theoretical problems related to electrets. But it was only in 1921

that Eguchi (1) actually received and investigated electrets. Eguchi's electret was a thermoelectret. Selenyi (24) pioneered on the injectionof electrons or ions into insulators. Nadzakoff (25) of Bulgaria discovered photoelectret in 1937. In 1950's, a number of charging methods depending on the application of high energy ionising radiation were devised. Bhatnagar of India invented magnetoelectret in 1960's. Recently, he has discovered optical magnetoelectret. Besides charging of insulator films with electron beams charging by liquid contacts is also receiving attention.

Preliminary explanations of the phenomena of charge-storage and transport in electrets came from Eguchi (1), Heaviside (2) Mikola (26), Admas(27), Gemant (9), Gross (28,29), Swann (30), Gubkin (31), Wiseman and Feaster (32), Perlman and Meunier (33). Further insight into the nature of charge retention was achieved from the studies of Gerson and Rohrbaugh (34) which indicated that carrier trapping could play an important role in electrets. The work on photoelectrets was extended by Kallmann (35) and by Fridkin and Zheludev.(36).

Dramatic progress was made by the introduction of

the thermal depolarization method, first introduced by Randall and Wilkins (37). This method was applied to the case of dipole polarization by Buccietal (38). A host of recent work (39-51) has been devoted to the application of Ionic thermal conductivity method or related thermally stimulated current (TSC) technique for investigating dipolar and space charge phenomena respectively (52-57). These studies have culminated in a very comprehensive treatment by Vanturnhout (58). Much of the newer work has been done on polymer electrets due to the fact that these show extremely good charge-storage capabilities and are available as flexible films.

At the end, it may be mentioned that round about 1980, TSC was utilized in discovering the effects of doping on polymeric films electrects, in particular, in India

1.5 Applications

Permanent charge storage property of electrets has been utilized in wide variety of applications. They reach from the technical areas to the biological and medical field and are in various states of research, development or production.

Some of the oldest practical devices of this kind are

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electret transducers. In 1962 microphones (78-84) with polymer electrets were introduced which gained widespread commercial acceptance. An other field of great importance is electrophotography. More recently introduced electret devices includes gas filters, motor's, relay switches, optical display systems and radiation dosimeters. Commercialized gas filters use Corona (85) charging. External field of electret is used in relay switches. Dosimeters are based on radiation induced conductivity. Electroacoustic tranducers utilize piezo and pyroelectric effects of polymer electrets. Electret characteristics of human and other bones and blood-vesselwalls and enhancement of the blood compatibility of polymers by negative charge deposition have opened great future potentials. It seems that its use in phenology may be possible. A few applications are explanined in fig 1.5.1.

1.6 Brief theory of thermoelectret

Dipolar component of polarization $P(t)$ is controlled by Debye equation. In few special circumstances one has (58)

$$P(t) = \in_0 \in E\,[1 - exp\{-\gamma(T)\,t\,\}]$$

$$and \; \gamma(T) = \gamma_0 \; exp\,(-A/kT)$$

Where   t = Time,

Fig 1.3.1 Electret microphone, headphone and motor

Metal layers

Microphone diaphram

Polymer

ε

E

σ

Air Gap

E_1

Metal back plate

R

V +

Enlarged small section of on electret microphone Horizontal dimensions musch larger than vertical.

Metal layers

Front plate

Front plate

Monocharge nonmetolized electret films

Back Plate

Back Plate

Metallized electret films

Conventional Double-electret Transducer

Single monocharged electret Transducer

Push - Pull electret head phones
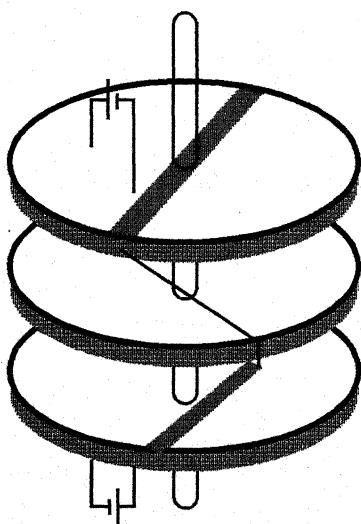
Slot- effect motor

T = Kelvin temperature

γ = Dipole-Relaxation frequency

γ_0 = Preexponential factor

A = Dipolar activation energy

$\in_0$ = Permittivity of vacum

$\in$ = dielectric constant of the matierial

E = electric field and

k = Boltzmann's Constant

Space charge cantribution depends upon the conductivity $\sigma(T)$ of the dielectric and is given by Arrhenius relation as

$$\sigma(t) = \sigma_0 \, exp \, (-B/kT)$$

here B = activation energy for conduction. Charge injection from electrodes is governed by schotty emission which yields a current density

$$j = j_0 \, exp \left(-\frac{\Delta\phi - \beta E^{1/2}}{kT}\right)$$

where $\Delta\phi$ = difference in the work function between electrode and the dielectric, and β = Schnottky

$$\text{Coefficient} = \left(-\frac{\varepsilon^3}{4\pi\varepsilon_0\varepsilon}\right)^{1/2}$$

here e = electronic charge

However, in highly insulating materials with strong trapping, a time dependence of the injection current is observed.

In this case the injection is essentially limited by trapfilling, either at interface or in the bulk, and the injection current is often discrived by

$$J \propto [E(t)]^m \, t^{-n}$$

while the exponent n is generally below unity but approaches this value as the trapping becomes increasingly effective, m is expected to exceed 1. For polymers typical values of n are between 0.1 and 1 and for m between 1 and 3 (86). At high fields injection of charges is very important (87,88)

All the three mechanisms depend upon temperature in the same manner. It introduces several complications.

1.7 Theories of Photo Electret-

Phenomenological theories of photo electret have been proposed by Kallman and co-workers (89-93). Fridkin and Zheludev (94-96) Chetkarov (97) and Adirovich (98). The

conclusion of these theories agree qualitatively with some of the experimental results, although the approach towards the mechanism of polarizationis different. Tartakovskii Rekhalova (99) and Kalabukhov and Fishelev (100) proposed that illumination produces transitions of electrons from the valence band to conduction band, where they move under the influence of applied electric filed. The electrons then leave the conduction band and are trapped at localized levels lying below the bottom of the conduction band. Freeman, Kallmann and Silver (89) suggested that an electric polarization is due to an inhomogenous charge distribution brought about by an external filed acting on free charge carriers. Internal polarization effects are described in terms of the 'frozen in' charge distributions. The buildup of polarization occurs during external field application while the photo conductivity is in a state of excitation. This separation persists after excitation and field removal because of trapping processes. For these frozen-in charge distribution, static models have been developed. Experiments (93) show that two fundamentally different internal charge distributions can develop barrier and bulk polarization. Barrier polarization is produced when surface resistive layers interact strongly with charge transport through the sample. The free positive and negative charge carriers accumulate near the electrodes because of high resistive layers at the photo·conductorelectrode interfaces. If

these two resistive layers are of the same magnitude, the barrier polarization leaves the sample electrically neutral. Furthermore, it is not necessary that the sample be uniformly excited during polarization. In bulk polarization the more mobile carriers are atleast partially removed from the sample with the less mobile carriers remaining in a fairly uniform distribution over the bulk of the sample. According to Fridkin et al (91), the photo polarization state produced by the application of field and light, is based on the scheme of electronic energy levels and the investigation of space charge in photo-condition provide a basis for understanding photo-electret mechanism.

It may, however, be pointed out that a theory which successfully explains the behaviour of thermo-electrets, might prove quite inadequate to explain that of others.

Although a number of therories have been suggested by various workers, yet none of them is completely satisfactory. Thus electret state of materials provides a wide and rewarding area of research.

1.8 Material and the form of samples:-

Organic insulating materials (101-145) have been the subject of considerable interest due to their wide applications in a number of devices. In recent years the studies of these materials in the film form (146-149) have attracted the attention of

investigators due to their application in micro electronics and electrets in a number of electrical devices. Due to their small size, thin specimens are preferred to the crystals of bulk material. Thin samples have still wide range of application as compared to bulk organic crystals.

Several techniques are available to form the films of organic materials (147-156). Among them are thermal evaporation (157), sputtering techniques (158) or chemical deposition methods (159). The films formed by thermal evaporation result in degradation of materials. Such films also suffer from the presence of pin holes and voids. The problem of pinholes can be controlled in films prepared by sputtering or chemical deposition. The problem of degradation if the material can be overcome in case of polymeric organic materials (160-161).

Polystyrene (PS) doped with iodine has been chosen for the present investigation.

PS is an amorphous polymer. Its supermolecular organization is explained in terms of cluster structure. By cluster Ubbelode (162) means the regions (domains) that have a denser packing of molecules (or their parts) and a more ordered arrangement of them in comparison with the main looser and unordered mass of a substance, it is natural that the density of a cluster should be some what greater than the average density of a

substance. At the same time clusters are less ordered and less densely packed domains than crystallites. Clusters exist that in definite conditions are capable of having a more ordered arrangement of their moleculer. i.e. they are capable of crystallization. On the other hand, the existence of clusters that in principle do not crystallize is also possible. Since regular packing of the particles in three dimension in this case is absent, then when cooled from melt, anti-crystalline clusters can not continue to grow unlimited by without the appearance of voids for dislocations. If the model proposed by Ublelode (162) is applied to polymers, it can be assumed that in addition to crystalline regions, a polymer may also have crystallizing and non crystallizing clusters. In this connection a polymer may be considered as a complex of separate domains forming different parts (by volume) of the total volume of a polymer and organized in different ways. From that stand point, PS can be considered as a complex of different kinds of non crystallizing clusters among less ordered and looser regions.

The glass transition temperature is the most important characteristic temperature of amorphous polymers. The concept of the glass transition temperature of polymers was introduced by Ueperreiter (163-164). There are different definitions of this temperature, two of which are in the greatest favour and are the most correct. By the glass transition

temperature Tg is meant the temperature at which the viscosity of polymer is 10^{13} poise (165). On the other hand, it is interpreted as the temperature below which segmental motion of the polymer molecules is frozen. There are many experimental methods for determining Tg (165-167). The most dependable one is its determination according to the temperature dependence of the specific volume on condition that the sample under study is subjected to thermostatic control for a sufficient time at each temperature point at which measurement are made. Acoustic methods are successfully used for determining Tg (168-170). It is the most correct to determine the Tg according to the change in the temperature coefficient of velocity of sound, in the glassy state with an unchanging nature of the molecular mobility the velocity of sound depends linearly on the temperature. Above Tg, When unfreezing of segmental mobility of the micro-Brownian type begins, the temperature coefficient of the velocity of sound sharply changes. For PS the velocity of sound changes most greatly at $105^{0}C$ (171) According to the data of dilatometric measurements, the Tg is also equal to $105^{0}C$ (171). Wada and his Callaborads (172), using the temperature dependance of the specific volume, found temperature transitions at $105^{0}C$ in PS. This shows that the Tg of PS is $105^{0}C$.

1.9 Dopant Material :-

One way of modifying polymers used to improve their properties is the addition of impurities. Plasticizers are introduced in to the polymers to decrease the effectiveness of intermolecular (interchain) interaction(173). The mciroscopic effect of plasticizing usually manifests itself in a reduction of Tg. Both low and high molecular substances are used as plasticizers. The plasticizing action depends on the chemical structure, size and shape of the plasticizer molecules (174). Gibbs and Marzio (175) showed that the effectiveness of the plasticizer depends, to a considerable extent, on the conformation set of its molecules. Plasticizers whose molecules can take on a greater number of conformations lower the Tg of polymer to great extent.

Certain applications of polymers in solid devices have necessitated increasing of their electrical conductivity. Several workers have reported increase in conductivity of polymers due to dopping of them with several impurities. Polybutadine has been doped with chloranil and an increase in conductivity and carrier mobility has been observed (176). Low and high density polyethylenes have been doped with halogens and the largest increase in conductivity has been observed due to incorporation of iodine (177) Recently PS has been doped with acrylic acid (178) chloranil (179), copperthalocyanine (180),

iodine (68), pyrene (69) ferrocene and anthracene (64) and a marked increase in conductivity of the polymer has been observed. These result show that the conductivity of polymers can be greatly affects by dopping them with suitable impurities. Both inorganic and organic (181, 185) impurities can be used to modify the electrical conductivity of polymers. Inorganic impurities have more profound effects than organic imurities. Hologens are known to form polymer halogen complexes (11) with rigid matrices. Iodine is an strong electron acceptor type impurity and can affect greatly the conductivity of polymers. For the present work iodine has been chosen as the material to be incorporated in PS.

1.10 Methods of investigation:-

The knowledge of electrical conduction is essential in order to understand the electret forming characteristics of the material. The bulk properties of the electret are investigated most directly by the sectioning technique (11). But planning the surface of a polarized dielectric is a drastic operation. It generates new surface charge by triboelectric and breakdown effects which falsify the results of surface charge measurements made with the dissecrtible capacitor. Preferable is the measurement of thermally stimulated current (183-187). Photo electret state in the material can by investigated by measuring photo depolarization current (188-192). There is a definite co-relation between electrical

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conductivity and the dielectric properties of material (193-197)
Therefore, the work reports on electrical conduction thermally
stimulated current, photo depedarization current and dielectric
properties of iodine doped PS films.

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Chapter-2
Experimental Details

EXPERIMENTAL DETAILS

2.1   Film Preparation Techniques :-

Materials can be casted into films by thermal evaporation (198,199) sputtering (200, 201) and chemical deposition methods (202, 203). In thermal evaporation, solid materials vaporize when heated to sufficiently high temperature. The condensation of vapour on to a cooler substrate yields films. Evaporation can be carried out by a flash, arc and laser or by resistive, exploding wire, RF and electron bombardment heating. The ejection of atoms from the surface of the material by bombardment with energetic particles is called sputtering . If ejection is due to positive ion bombardment, it is referred to as cathodic sputtering. The Sputtered atoms can be condensed on a substrate to form a film. Because of the high pressure of the gas used and high sensitivity to contamination is commonly used glow discharge sputtering, the technique has generally been termed dirty. Sputtering can be achieved by low pressure, RF, ion beam and reactive sputtering. Electro and electroless deposition and anodic oxidation are chemical methods to deposit films. In chemical vapour deposition technique, a volatile compound of the

substance which is to be deposited, is vaporized. The vapour in thermally decomposed or reacted with other gases, vapours of liquids at the substrate to yield non volatile reaction products which deposit atomistically on the substrate. Technology of film preparation has been reviewed by chopra (204).

The irradiation technique for the preparation of polymer films is high energy technique. Similarly RF sputtering of polymers is also a high energy process. In these high energy processes the cross linking of the polymer chains is highly probable. The films so formed show high dielectric losses and degradation with time. These films are, therefore, not suitable for practical applications. Films of polyvinylchloride acetate co-polymer (205) have been prepared by spreading cyclohexanone solution of the polymer over a water surface. Spivack (206) has prepared parylene (the generic name of a family of polymers based on poly-p-xylene) films by using the vapour phase deposition process which has been described by Gorham (207). The films thus formed have excellent mechanical, physical, electrical and barrier properties. They are virtually inert to most acids and bases and are insoluble in most organic solvents below 170^0C. The isothermal immersion technique (208, 209) on the

Fig. 2.1 ISOTHERMAL IMMERSION APPARATUS
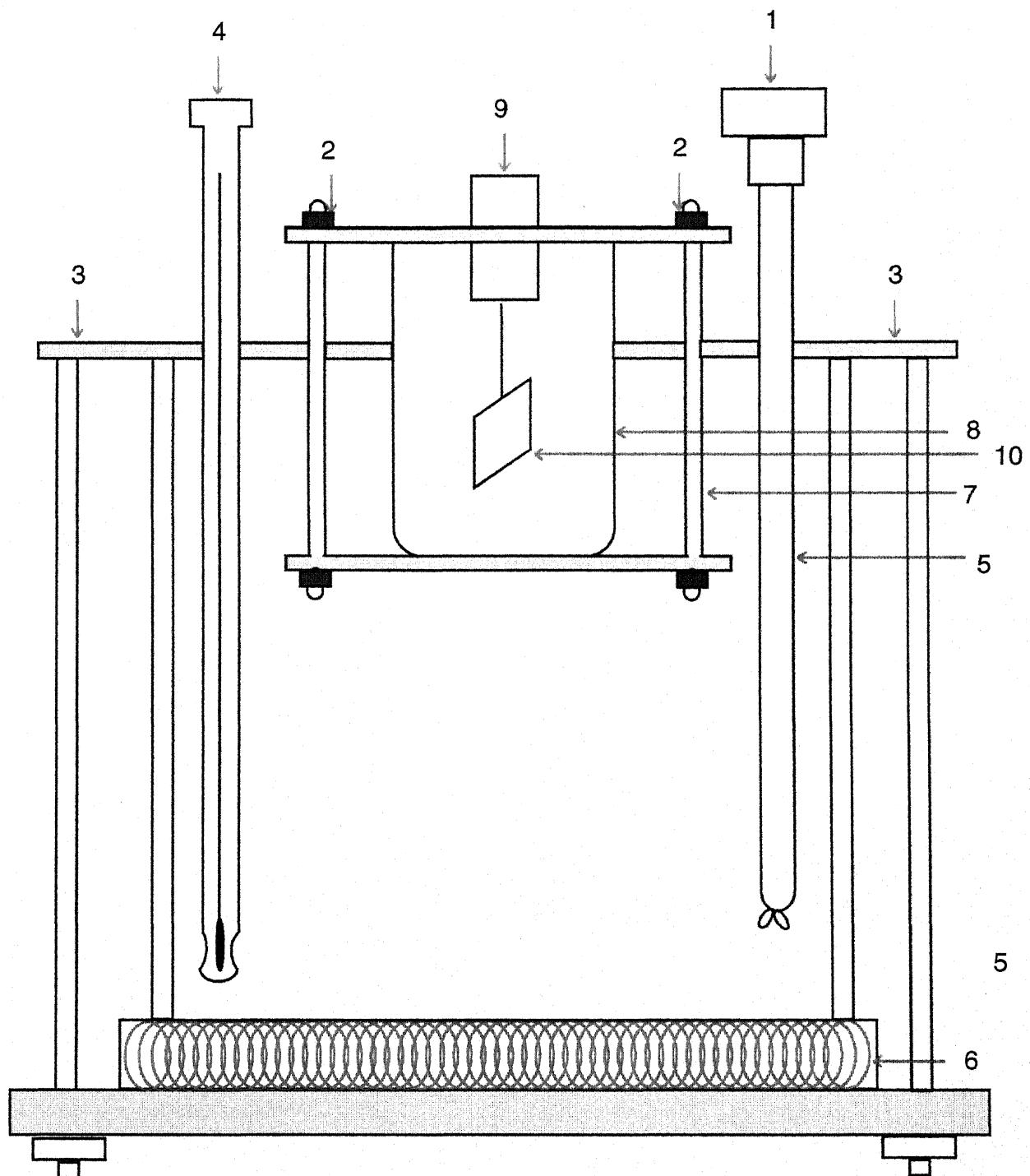
1 Motor 2. Substrate Holder Assembly Support, 3. Oil Bath Cover, 4 Thermometer
5. Stirrer, 6. Heating Coil, 7. Polymer Solution Vessel Support, 8. Solution Container,
9. Substrate Holder 10. Substrate

other hand, appears to be simple and powerful technique for obtaining durable and useful polymer films. Isothermal immersion technique has been used by several workers (65, 210) to prepare ploymer films. In this method, the growth of the molecular chains on the substrate is predominantly lateral. The molecular chains or the clusters of the chains observed on the substrate attain a definite equilibrium size. These clusters do not significantly increase in size as the equilibrium thickness of the films increases or their number increases. The clusters tend to deform in one particular direction and the extent of deformation increases as the equilibrium film thickness increases. The clusters of the molecular chains have a preferred direction of orientation. Films of higher equilibrium thickness have more of amorphous areas surrounding the crystalline area.

It is clear from what has been stated above that the growth of the films from solution occur by absorption controlled nucleation of molecular chanis on the substrate and the further growth occurs by the attachment of more chains on the already adsorbed chains forming a cluster of chains. The adsorbed chains and subsequently the clusters of chains adjust them selves laterally on the substrate.

Film Preparation :-

Commercial grade PS was used in the work. PS was dissolved in cyclohexanone. 100 mg of iodine was desolved in 10ml cyclohenanone. The required number of dorps of iodine solution were added to the PS solution with an 1 ml pipette while stirring. Let us designate the films as I_1, I_2 etc. to mean that they were prepared by adding one, two etc. drops of iodine solution in to the PS Solution. This method of doping in which iodine solution is mixed in PS solutionn is termed common solvent method. All foils were cleaned by rubbing them with cotton and then bykeeping them immersed in benzene. The cleaned foils were stored in pure alchohol. Isothermal solution immersion growth technique of preparing the films involves isothermal immersion of the substrate in to the polymer solution held at a particular temperature for a certain time. The apparatus used to prepare the films is shown diagrammatically in Fig. 2.1.

Polymer solution was immersed in the oil bath. The temperature of the oil bath was kept constant at 30^0C. The substrate was held in the constant temperature bath. After bringing the solution and the substrate at 30^0C, the sustrate was immersed

in the solution for 10 minutes. The films were dried by keeping them within the thermostat at 30^0C for more than 3 days.

2.3 Evaluation of Film thickness:-

The thickness of the film was extrapolated by measuring its capacitance at 10 KHz and taking the permittivity (ε) value equal to 3.

2.4 Vairatioon of electrode forming material :

Films were grown on Al substrates. To sudy the electrode effect, films were also grown on Zn, Ni and Cu substrates. The substrate acted as an electrode and the other of Al 1Cm^2 in area was pressed on to the film.

2.5 Electrode Assembly :

A pressed on electrode assembly was used in the investigation. It is diagrammatically shown in Fig. 2.2. The film alongwith the substrate was kept on the bottom teflon sheet so that the substrate contacted with the teflon. An Al electrode of 1 c Cm^2 in area surrounded with the guardring to avoid the surface effects, was pressed on the film with the help of the flyscrew. The contact of the flyscrew with the electrode was insulated with a teflon disk. The substrate acted as another electrode.,

FIG 2.2 ELECTRODE ASSEMBLY

Fly Screw

Brass frame

Electrode

Film

Teflon

Substrate

FIG 2.3 ASSEMBLY FOR PHOTO EXPERIMENT

Fly Screw

Electrate

Taflon

Film

semitranparent
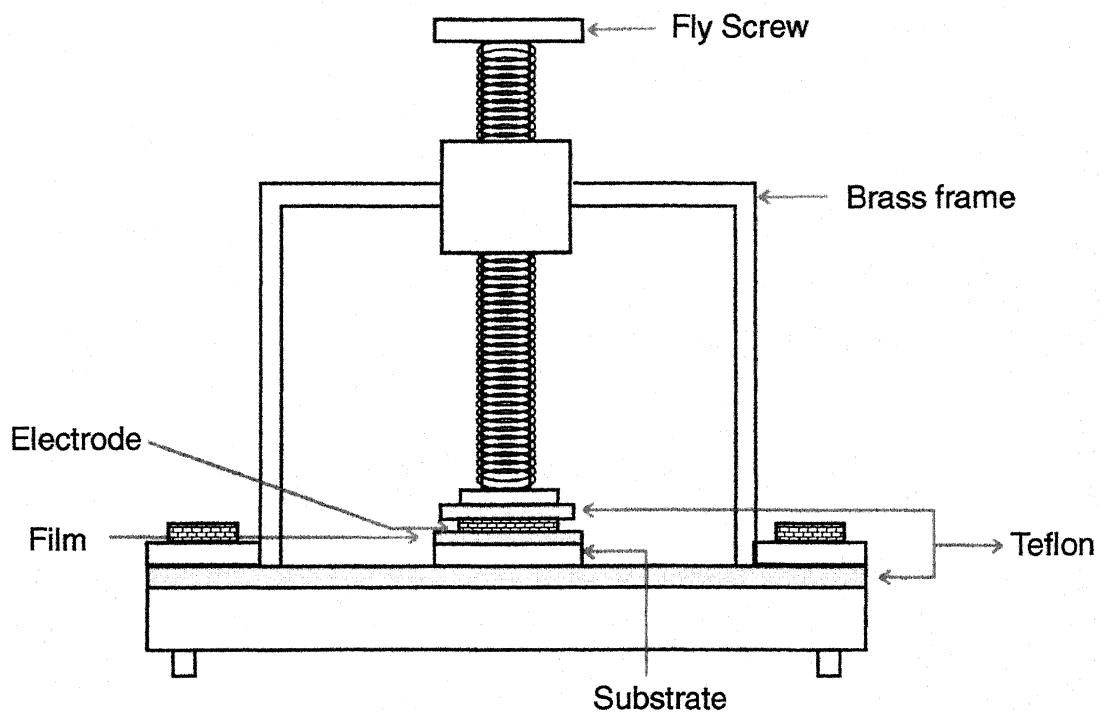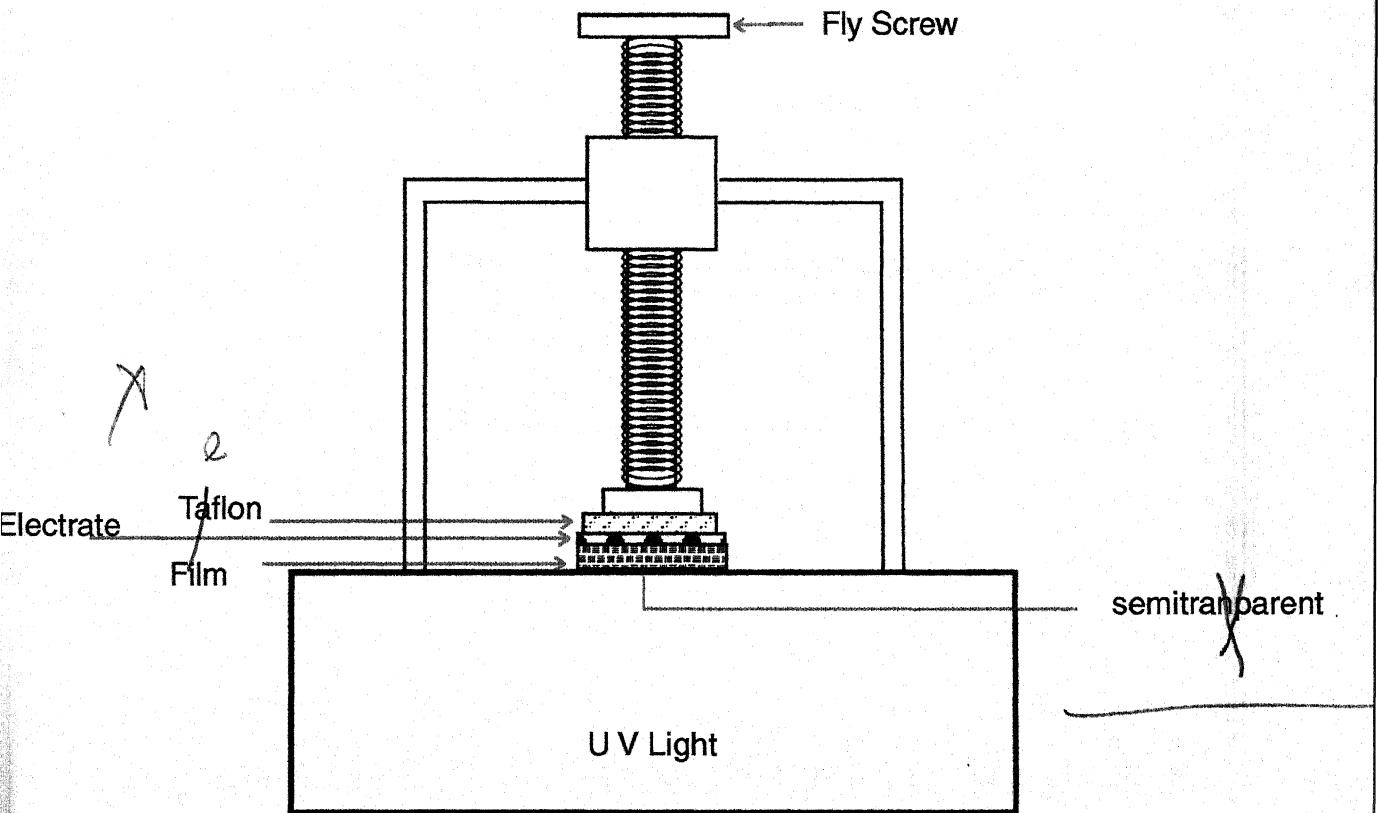
U V Light

2.6 Assembly for photo experiment:

Assemblly used in photo-polarization and depolarization expriment is schematically shown in fig 2.3. UV light of wavelenght 1518 A^0 from a 15 watt lamp was incident on the film through a semi-transparent silver electrode. The substrate acted as the other electrode.

2.7 Role of Air in the present experimental setup.:

For fundamental studies vacuum deposited electrodes are preferable. However, in the present investigation pressed on electrodes have been used. In case of pressed on electrodes the contact between the electrodes and the polymer is imperfect and there are air spaces between them, in which at high field strenghts townsed breakdown will occur, so that ions or electrons from the air are injected into the polymer. The homocharging by breakdown of the air is deliberately intensified in the manufacture of electrets (58). This development is logical, because the deposition of homo charges from the air is a much faster process than the hetero charging by dipole orientation and space charge motion with in the polymer.

2.8 Electrometer:

The " Electronics Corporation of India Limited" Varactor Bridge electrometer type EA 815 is high performance electometer amplifier specially designed to measre very small direct current, low DC potentials from high impedance sources, small charges and high resistances.

The extremely rapid response combined with its good stability and low drift characteristics, makes it a useful instrument in nuclear research, electrochemical and bioelectric measurments, spectrographic and electrophoretic studies, in measurement of grid currents of electrometer tubes and the contact potentials.

a) Specifications :-

Voltage Ranges	: 10mV, 30mV, 100mV, 300mV, 1V, 3V & 10V of both polarities.
Inpute impedance (Voltage measurement)	: 10^{14} ohms in the open position of the input resistance switch.
Current Ranges	: 10^{-5} to 10^{-14} A. F.S.D. Both polarities in 28 overlapping ranges.
Input Resistances	: 10^6, 10^8, 10^{10} and 10^{12} ohms

selectable by a front panel Input Resistance slector switch.

Input Sensitivity : 10^{-16} A per division for current measure ments.

0.1 mV per division for voltage measurement.

Accuracy of current Measurment : 3% in 10^6, 10^8, and 10^{10} ohms ranges 5% in 10^{12} ohms ranges.

Accuracy of Voltage Meaurements. : Built-in meter: 1% ±. o.1mV on all ranges.

(at a Constant A.C. Voltage)

Input Time Constant : 15 Seconds in 10^{12} ohms range. 10 seconds in 10^{10} ohms ranges reduces to insignificant time in other (agnes).

Zero stability : 0.3mV/12 hrs.

Short Term fluctuations : 0.1 mV r.m.s.

Effect of ±. 10% mains : 0± 0.5 mV

(Voltage Variation).

Input Power : 210-250 V, A.C. 50 Hz.

b) Brief Circuit Description :-

The EA 815, Electrometer Amplifier is intended for

the measurement of DC potentials across high source resistances, very small direct currents, high resistances and very small charges. All the above measurements being carried out in terms of potentials.

The ranges covered by the instrument are 0-10mV through to o-10V of either polarity. The input resistance being greater than 10^{15} ohms and the zero drift of less than 0.3mV in 12 hours. The input terminal is specially selected for its high insulation characteristics.

The circuit comprises mainly of two parts, the power supply and the Varactor Bridge Electrometer.

1.   The Power supply provideds +15 and -15V regulated for the operation of the circuitry. Diodes D1 and D4 constitute a rectifier bridge across the 16-0-16V winding of the mains transformer with the centre tap as the reference. Capacitors C5 and C6 provide the filtering for the two lines. The two supplies are regulated using series type regulating circuits comprised of the series transistors Q1 and Q4, error amplifiers Q2 and Q3 and reference voltage zeners D5 and D6 repectively.

2. The Varactor Bridge Electrometer is an extremely low input bias current and high input impedance operational amplifier capable of high quality performance. In principle, the Varactor Bridge Amplifier design is similar to that of the vibrating read electometer but with the inherent advantages of the solid state circuitry. It uses a hybrid integrated circuit chip (type 310 K-of Analog Devices) resulting in great compactness and reliabilitiy.

c) Operational Controls :

Input : Highly insulated teflon input connector receives input to be measured.

Input Resistance : Rotary switch selects input resistances as indicated the panel i.e. 10^6, 10^8, 10^{10} and 10^{12} In 'OPEN' positions, terminals will be available at the switch for connecting a capacitor of known value from the external circuit for charge measurements.

Mains : Switches ON the mains supply to the instrument when pressed. Glow of the pilot lamp indicates the presence of supply.

Zero Adjusting : 10 turn helical potentiometer to set the

electrical 'Zero' of the meter.

Range   : Rotary switch selects voltage ranges from 10V to 10mV as indicated on the panel.

Polarity   : Selects input polarity (+Ve or -Ve) and disconnects the meter from the circuit in OFF position.

Current-Voltage : Sets the unit for either current or volatage measurements.

Fuse   : 100 mA

d). How to operate the unit-

Before switching On the instrument make sure that the panel controls are as follows

i.   Current Voltage   : in Current Position

ii.   Range   : in 10V position.

iii. Polarity   : in "OFF" position

iv. Zero adjustment   : in mid position of the 10 turn helipot.

v.   Input socket closed with the metal dustcap provided.

vi. Input resistance in 10^6 position.

e)   Switching ON the unit-

i)   Connect the instrument to the mains supply.

ii) Set the input resistance switch to 10^6 ohms position and

depress the mains switch. Presence of supply will be indicated by the glow of the pilotlamp.

iii) After a warm up time of about a minute set the polarity switch to the required polarity. Now the meter will indicate Zero. If that is not the case the instrument has to be suspected for some fault.

iv) If zero is obtained at 10V position then turn the range switch to the most sensitive range step by step and adjust the electrical zero of the instrument by turning the zero adjust potentiometer. This zero adjust potentiometer will be seen to have effective control only in the lower voltage ranges.

v) Adjustment of zero on the meter in the most sensitive range will hold good for any other range for a particular input resistance selected.

Since there may be slight variation in the contact potentials for different input resistances selected, a slight re-adjustment of the zero setting may be necessary in each case.

Hence to obtain accurate measurements within the capability of the instruments, it is essential to check and adjust meter-zero prior to measurement every time the input resistor is changed. It is also essential to keep the range switch in 10V

position before changing the input resistance switch setting.

vi) It is essential to allow for one hour warm up time for getting the best results while measuring very low currents, charges and voltages.

vii) Now the insturment is ready for use.

f)   Current measurment -

Current of the order of 10^{-5} A to 10^{-16} A can be measured by measuring the potential across the known resistance connected in the instrument.

i)   Select the appropriate range by means of the range switch and the input resistance switch.

ii)   Remove the dust cap and connect the current source by means of the antimicro phonic high impedance cable to the input socket.

iii) Select the desired polarity by means of the polarity switch and adjust the zero by means of the zero adjustment potentiometer.

iv)   Apply the current and note the meter reading in millivolts or volts. Since the meter dial is calibrated in terms of voltage and input resistance is known by the switch setting, the current being measured can easily be calculated from those two

indications.

Temperature was measured with a precalibrated copper-constantan thermo couple. The thermoelectric e.m.f. generated was noted with a d c. micro-voltmeter.

Capacitance and losses were measured with a LCR systronics bridge incorporating an audiofrequency oscillator (form Toshniwal).

Dry cells of 1.5V and dry batteries of 9V were used to apply the desired voltage to the film.

2.9 Electrical Conductivity Measurement

Electrical conductivity of dielectrics is generally investigated either by heating the sample over a temperature range at a constant rate and keeping the applied voltage constant or by applying a voltage over a range keeping the temperature constant. Both the procedures have been adopted in the present investigation on electrical conduction.

Current voltage characteristics at different temperatures were traced by applying a voltage in the range 1.5-99V. When the film equilibrated at a particular temperature, a voltage was applied. The current was found to decrease first

rapidly and then slowly to reach the steady value. The voltage was varied in steps of 1.5V upto 9V and then in steps of 9V upto 99V.

Current temperature curves of various films were obtained by heating the sample at a rate of 1^0C min^{-1}. A voltage was applied to the film. The currents were noted at regular intervals of temperature.

2.10 Thermally stimulated discharge current measurement:

When the film equilibrated at a desired temperature, an electric field was applied for 30 minuts and was cooled with the field still applied to about 20^0C. The thermoelectret, thus formed, was short circuited for 2 minutes to minimize the stray surface charges. The electrets were heated at a linear heating rate of 5^0C min^{-1} to observe the thermally stimulated discharge current (TSDC).

2.11 Photo Depolarisation current measurment :

Photoelectrets were fabricates by applying an electric field for desired time in the presence of UV illumination. The electrets, so formed were preserved in dark for 1 minute to reduce stray surface charges and were depolarized by the same

radiation.

2.12 Capacitance and loss factor measurement:-

Dielectric properties of idoine doped PS were investigated by measuring simultaneously the capacitance and the loss factor over a wide range of frequencies and temperatures. When the film equilibrated at a desired temperature, the capacitance and the loss factor were measured by varying the frequency in audio frequency range.

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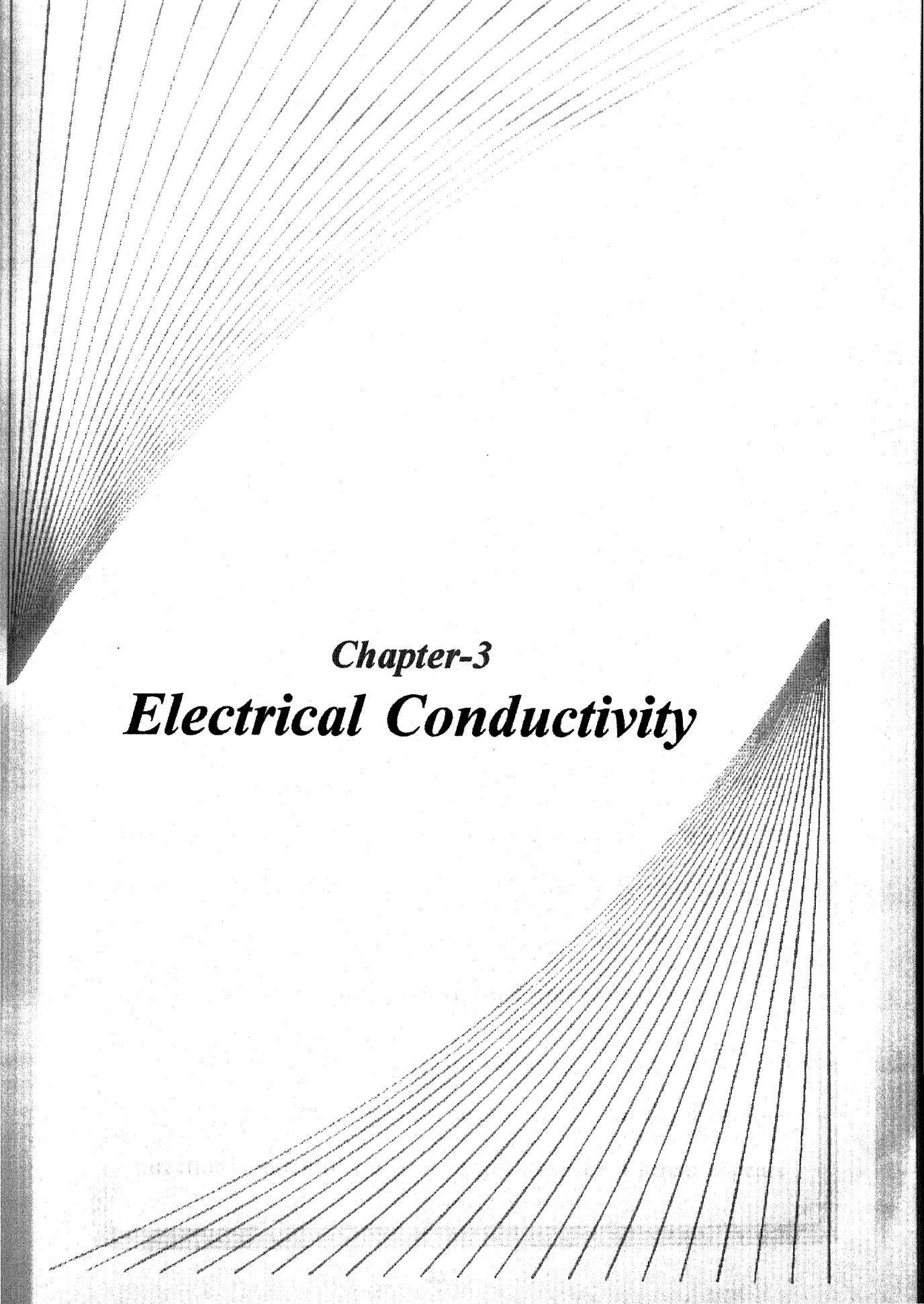
Chapter-3
Electrical Conductivity

ELECTRICAL CONDUCTIVITY

3.1 Introduction

Most of the polymers are considered to be insulators because they show low conductivity. (211-216) low dielectric loss and high break down strength (217). However, recent research in the field of polymers has led to the development of special type of high molecular weight materials which exhibits a conductance high enough to classify them as semiconductors (specific conductivity = 10^{-12} to 10^{12} ohm^{-1}Cm^{-1}) or even in some cases as conductors (218).

In the past several years, a good amount of work has been reported on electrical conductioon in polymeric materials (219-222) and various mechanisms (223-232) such as ionic conduction (233-235), Schottky emission (236-239). space charge limited conduction (239, 240) tunnelling (241). Poole-Frenkel mechanism (242), charge hopping (243, 244) and small polaron mechanism (245) have been proposed to explain the experimental results.

Electric current is an ordered (i.e., having a definite direction) motion of electric charges in space. Current appears

in matter under the effect of applied voltage. The charged material particles of the matter are being brought into the state of ordered motion by the force of an electric filed. Thus any matter will be conducting, if it contains free charge carriers. When ions move in an electric field, electrolysis takes place. Dielectrics with ionic conduction are also subjected to electrolysis but it is not so pronounced due to their high resistivity. A large quantity of electricity can be passed through them only during a long period of time, if a rather high voltage is applied. Electrolysis in dielectrics is more prominent at increased temperature when the resistivity of matter is reduced. The molecules of most of organic polymers can not be ionised but ionic conduction still takes place due to presence of impurities. Nonohmic conduction at high fields in ionic model is explained by diffusion over field perturbed potential barriers, by internal heating and by polymer structure modification by the field. The experimental temperature dependence and disproportionality between current and voltage are usually explained on the basis of temperature and field dependence of mobility. In that case, current-voltage curves follow a hyperbolic sine function, but it is not a definite proof of ionic conduction. In polymers with halogens in their molecular (218)

structure, electrical conduction is qualitatively proved to be ionic (234).

The fact that electronic conduction plays a role in polymers was established experimently by Seanor (246). To discuss electronic conduction, it is neccessary to investigate the generation of free carriers and their transport through the material. Several books and reviews (247-251) deal with the problem of carrier genertion. Contact limited emission was first studied for the metal vacuum interface. In this case three mechanisms of current flow may be distinguished. Thermionic emmision (252) (Schottky emission) occurs in the low field high temperature limit. Field emission (253, 254) (Fowler-Nordheim Tunnelling) occurs in the high-field low-temperature limit and is the direct quantum mechanical tunnelling of electrons from allowed states below the fermilevel in a metal into allowed states in vacuum. Thermal field emission (255-256) occurs when the dominent contribution to the observed currents arises from the tunnelling of thermally excited electrons through the narrow upper region of the image-force-lowered work-fuction-barrier. Murphy and Good (258) showed that each of these mechanism in limiting appoximation is observed under appropriate conditions of applied

field and temperature.

In polymers at or below room temperature, the density of free charge carrieres is extremely low and with an electric field, non equilibrium conditions can be achieved, which can be easily enhanced by injecting a charge through an ohmic contact. If the contact is equivalent to sufficiently large reserve of free charge, the current voltage characteristic does not depend on the manner in which the charges are generated but is strictly connected with the charge transport mechanism. Current-voltage curve is generally non linear on account of the two basic causes. At high fields the charges are accumulated between the electrodes (259). The presence of traps within the forbidden gap reduces the free charge density and produces a localized charge density within the polymer. The density energy distribution and the nature of the traps have a determining influence on current-voltage characteristic which also depends on the type of charges involved in the conduction process(260). Space charge limited current theory of Rose (261) has been modified by Lampert (262). Trapping sites exert a strong influence on the current flow i.e. on the concentration of free carriers and their mobility. Mobility values in polymers are very low suggesting strong trapping.

Phenyl rings and aliphatic or aromatic groups may be active traps. The trapping ability of unsaturation sides in the chain and the chain ends of pure polymer is confirmed. Similar conclustion are obtained by Perlman and Unger (263) in the studies of electron traps in irradiated polyethylene and teflon. Mobility values of polyethylene satisfy the relation for carrier hopping between localized sites. If the activation values of hopping are low 0.2-0.3 ev, hopping is connected with charge jumps brought about by motions of chain elements and the process is related to so called chain hopping mechanism while of greater values (0.5 eV) the so called trap hopping mechanism is involved. Martin and Hirsch (264) proposed energy traps 0.2-0.75 eV for polystyrene and 0.2-0.3 eV for polyethylene terephthalate, showing that both the mechanisms play a significant part. Life time of carriers in traps depends on th field. Thus band model with traps of various depths explains experimental results reasonably. However, the nature of charge carriers and trapping site has not yet been settled conclusively.

In polymers when H-atoms in the backbone chains are replaced by larger aromatic groups with π-electrons, the highest filled and the lowest empty molecular orbits are formed

from the substituents and the charge transfer occurs within the pendent groups where charge carrier density is higher due to higher affinity to electrons or holes. The role of backbone chain is less important. Taking into consideration that the overlapping of π-systems is small, the band width must be narrow. The band width depends on the method used but does not exceed 0.1 eV. This narrow band width is responsible for the fact that the electrons are for quite a long time connected with the particular π-system . The bonding energy of an electron to the potential well can be calculated. Thermal energy (Phonons) can be transferred to electrons, including thermally assisted hopping. This mechanism is called small polaron mechanism (265). In polymers conduction can be explained in terms of small polaron mechanism and in some cases as intrinsic phenomenon.

The trapping capability of a polymer can be greatly modified by dopping it with certain impurities (266-277). Carrier mobility in polymeric materials is increased by small molecules such as iodine (263). Recently Srivastava and co workers (68,69) doped polystyrene with several inpurities and found that the conductivity of the polymer is greatly enhanced due to doping of

Fig. 3.1, Effect of temperature, voltage and iodine concentration on transient currents in PS
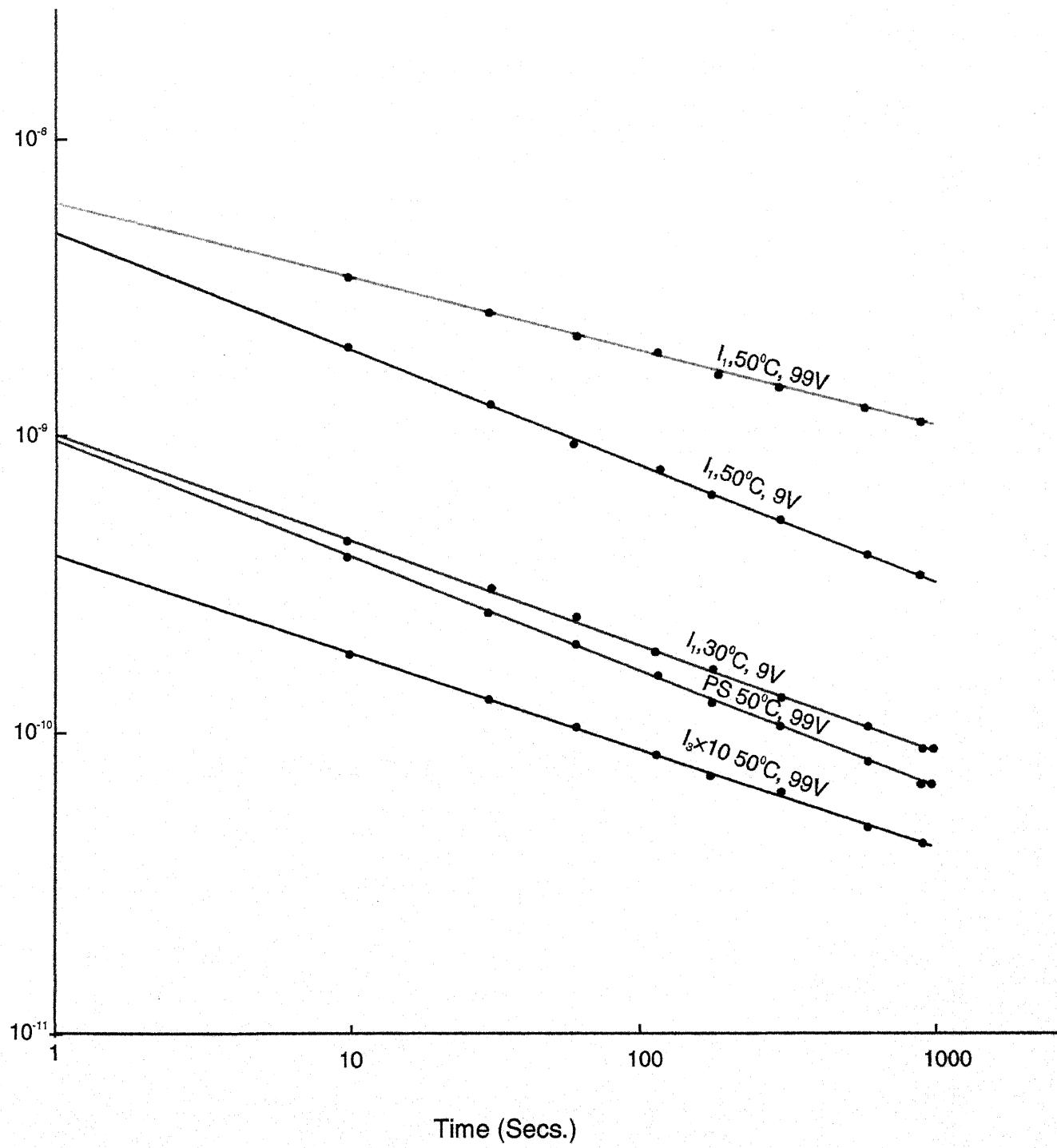
the matrix with iodine (68). The enhanced conductivity of the polymer has been interpreted in terms of charge-transfer complexes.

This chapter describes transient behaviour of current, current voltage characteristics and temperature dependence of current in iodine doped PS films.

3.2 Results

Application of a voltage to a polymer film causes current which is found to decrease first rapidly and then slowly. Transient behaviour of current was investigated in 20 μm thick films of PS, I_1 and I_3. At 50°C, I_1 gives ten times more current than PS. I_3 also gives more current but this increase is less. Current also depends upon applied voltage but the temperature dependence is more pronounced.

Current (J) versus time (t) on a double log plot yielded a straight line. the current may be described by

$$J(t) = A(T) \, t^{-b} \qquad \qquad .... (3.1)$$

When *b* is an exponent and A (T) a temperature dependent factor. Fig. 3.1 exhibits the effect of temperature, voltage and iodine concentration on transient behaviour of current.

Fig. 3.2. Electrode effect on schottky plots of I_1 at $50^{\circ}C$, effect of temperature on J-$V^{1/2}$ plots of I_1 and effect of iodine concentration on J-$V^{1/2}$ plots at $50^{\circ}C$
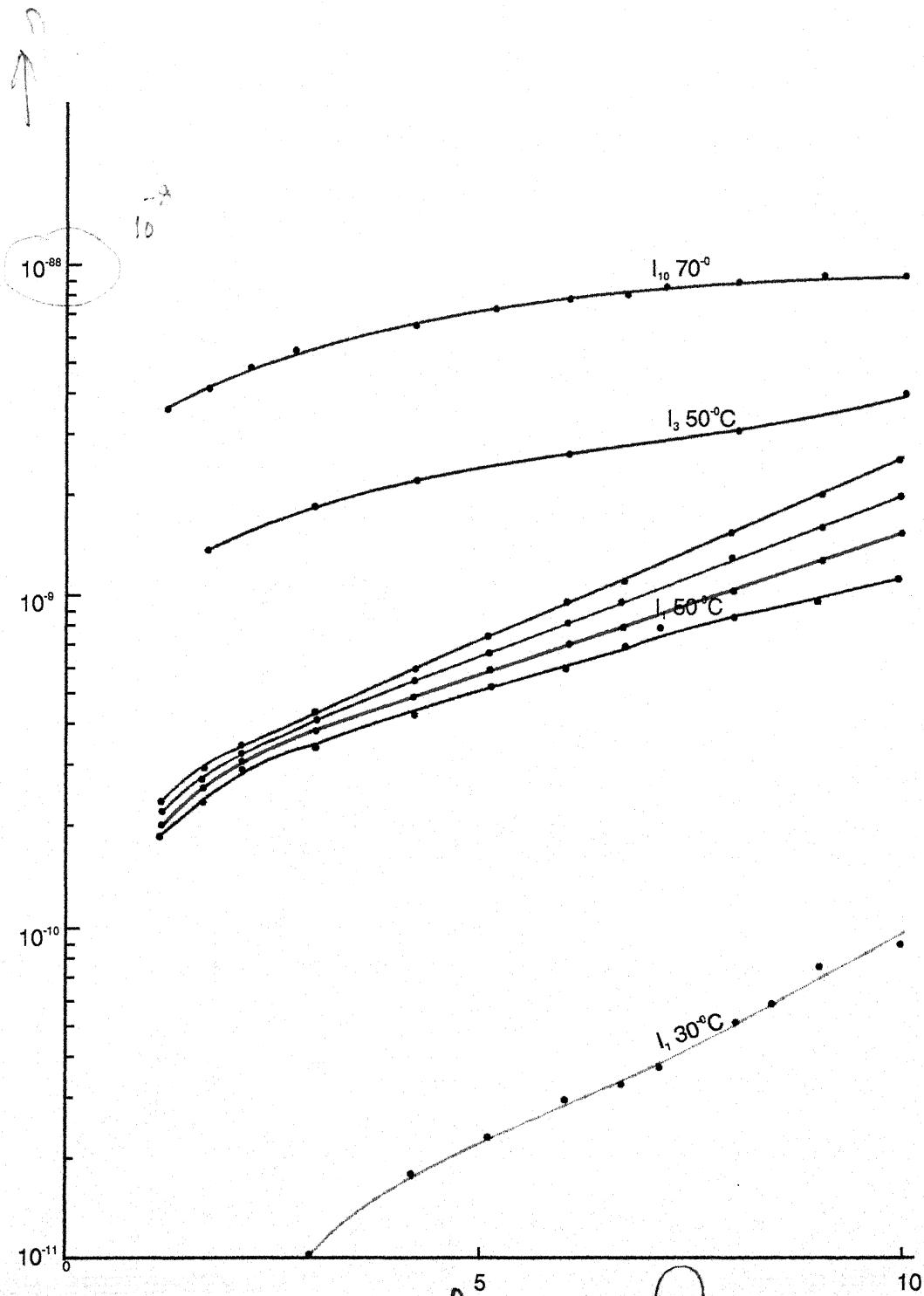
For different plots b ranged between 1.5-2.2.

Voltage dependence of current may be descirbed by

$$J(t) = K(t) V^p \qquad\qquad ... (3.2)$$

p is an exponent and K is a decay factor independent of voltage. Transient current was also found to depend upon electrode material.

Contacts provide an important source of carrier injection in poly-meric materials. To investigate the role played by contacts, steady state current - voltage (J-V) charactersitcs were traced at 50°C for I_1 in the configuration Al-PS-Metal. Al, Cu, Ni and Zn metals were employed to obtain a range of work function. The replots of J-V in the form fo J-V$^\cdot$ (schottky plots) are shown in Fig. 3.2. The figure also shows the effects of concentration and ~~temperatue~~ The plots when extrapolated in the backward direciton seem to originate from the samepoint. Therefore electrode dependence is rather weak.

Fig 3.3 illustrates the effect of thickness on J-V characteristics of I_1 at a constant temperature of 50°C. For the thicknesses of 20, 10 and 5 µm the J-V plots are linear. It is seen that slope of J-V plots increases with the decrease in the film

not obvious in Fig 3.3

Fig. 3.3, Effect of Thickness on Current-Voltage Characteristics of I, at 50°C
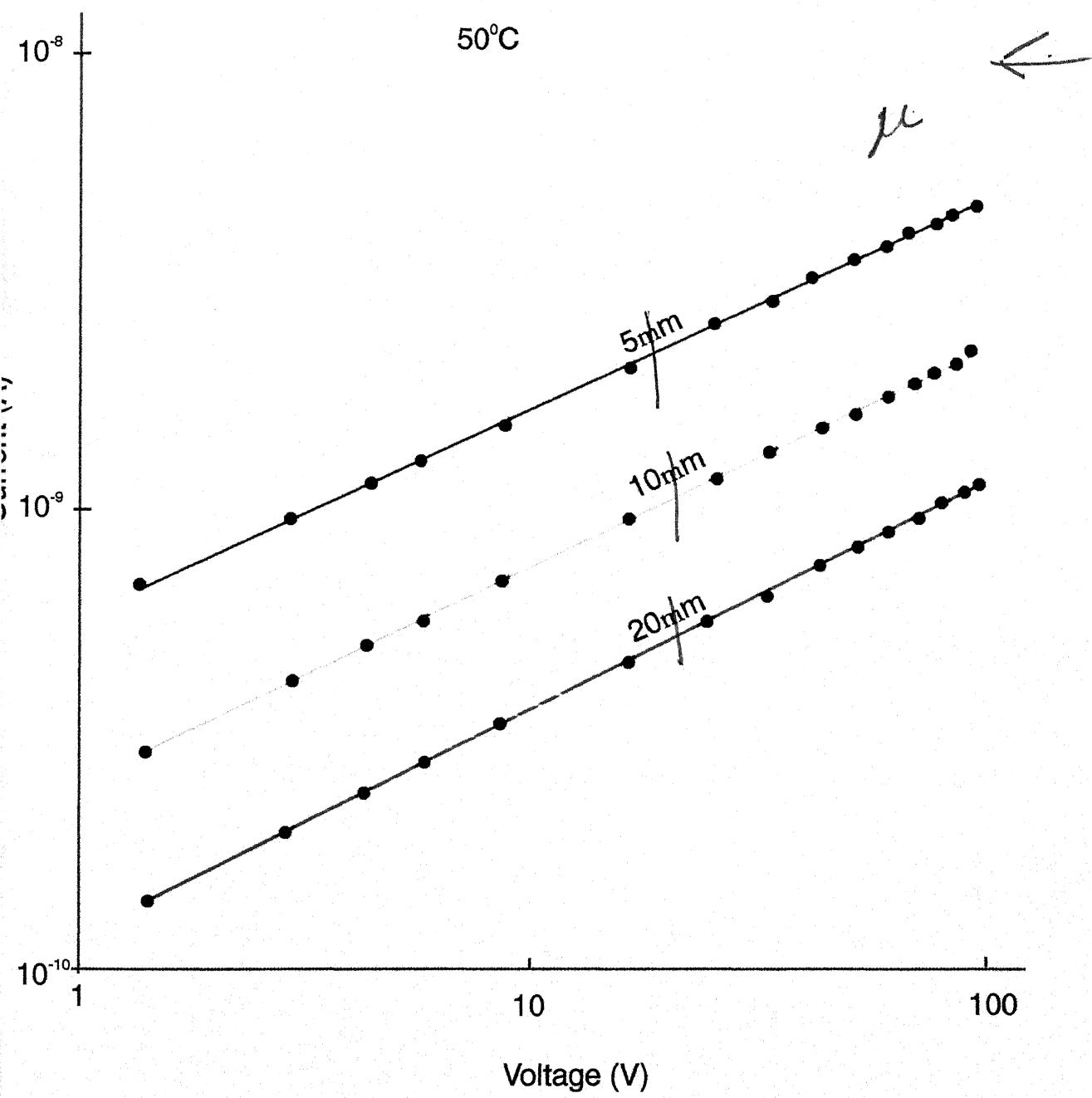
Fig. 3.4, Current Vs reciprocal Thickness Cube of I_l, at 50°C Voltage indicated on the plots
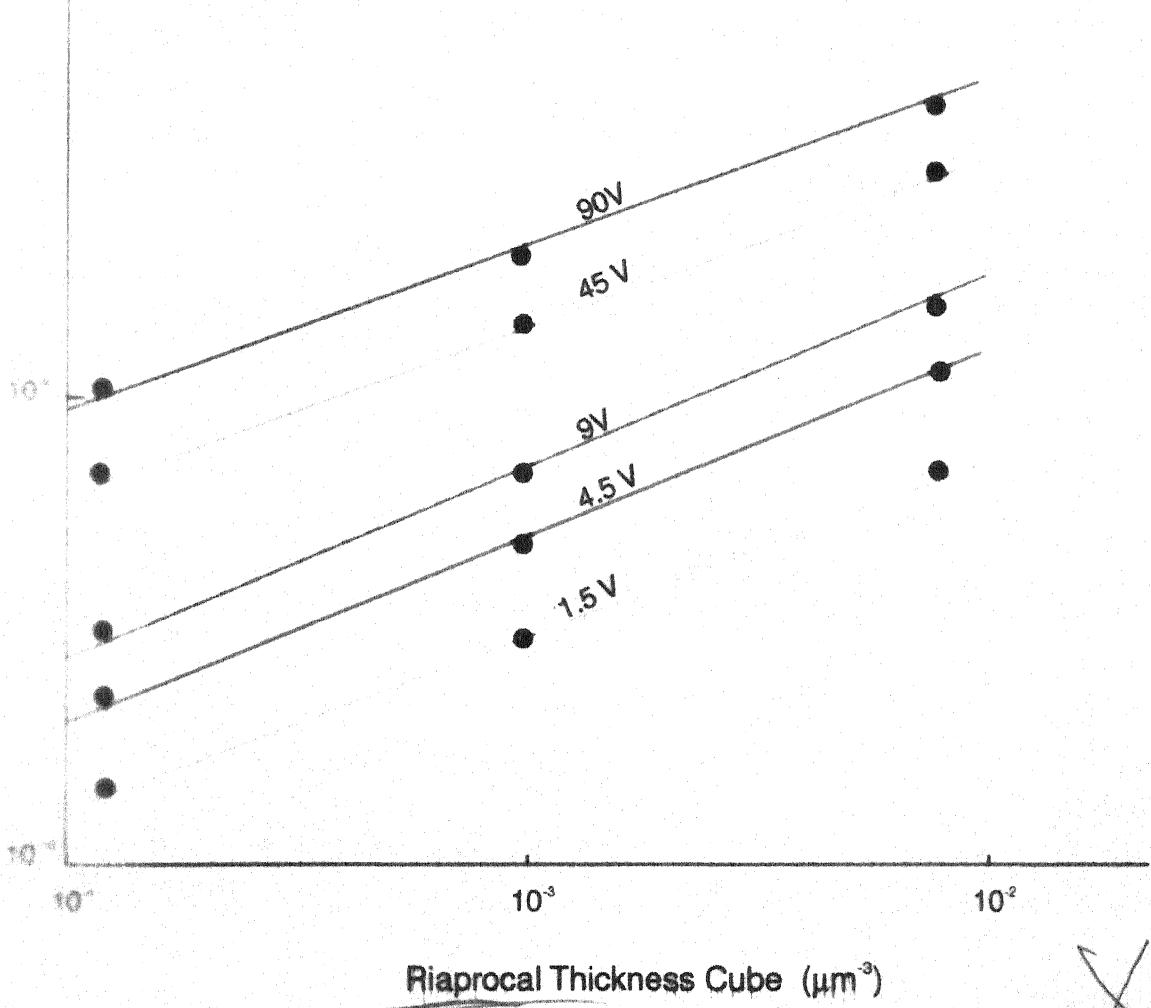
Fig. 3.5, Effect of iodine concentration on Current-Voltage Characteristics of PS
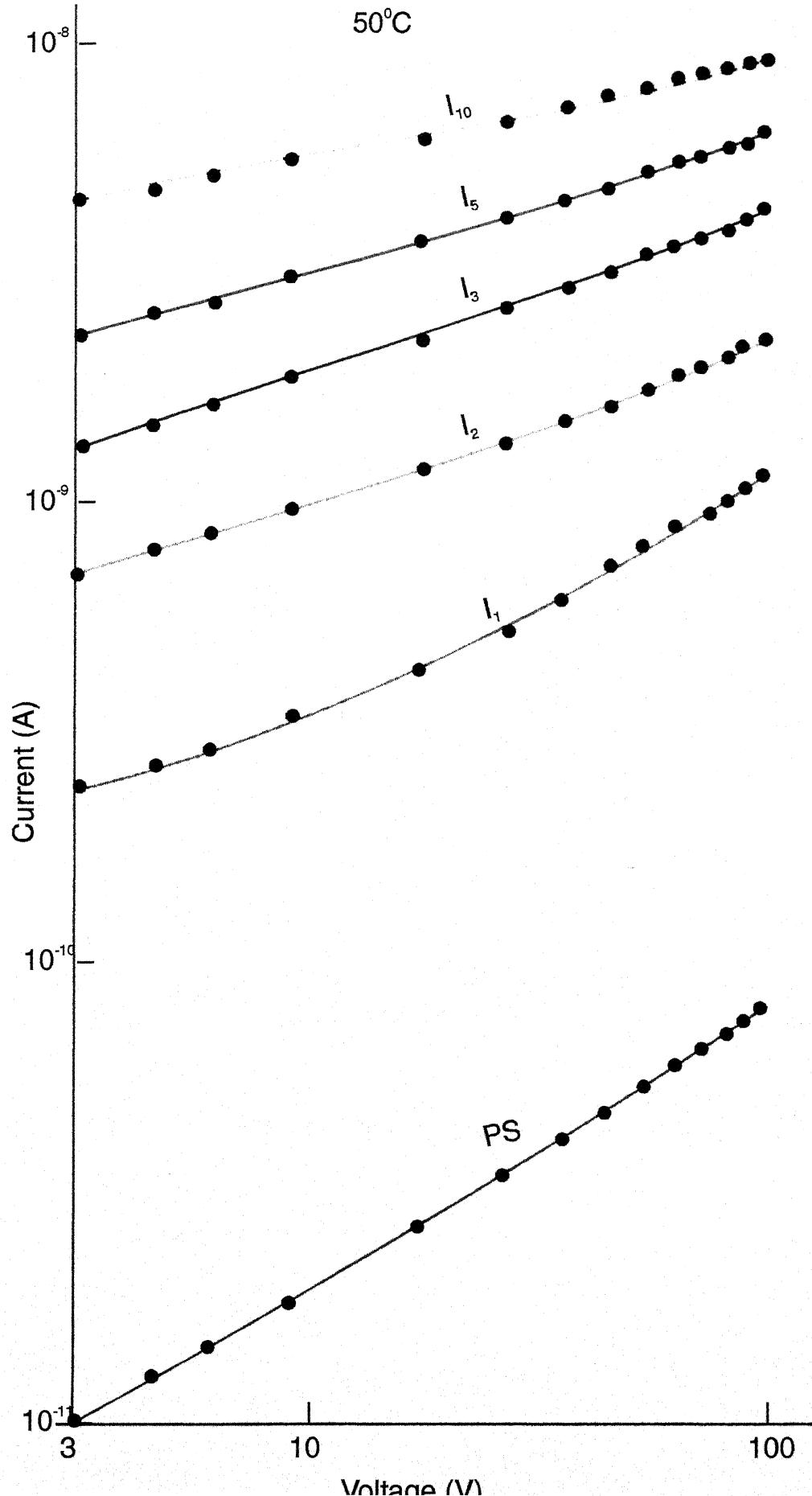
Fig. 3.6. Current-Voltage Characteristics of I,
at differnt tamperatures.
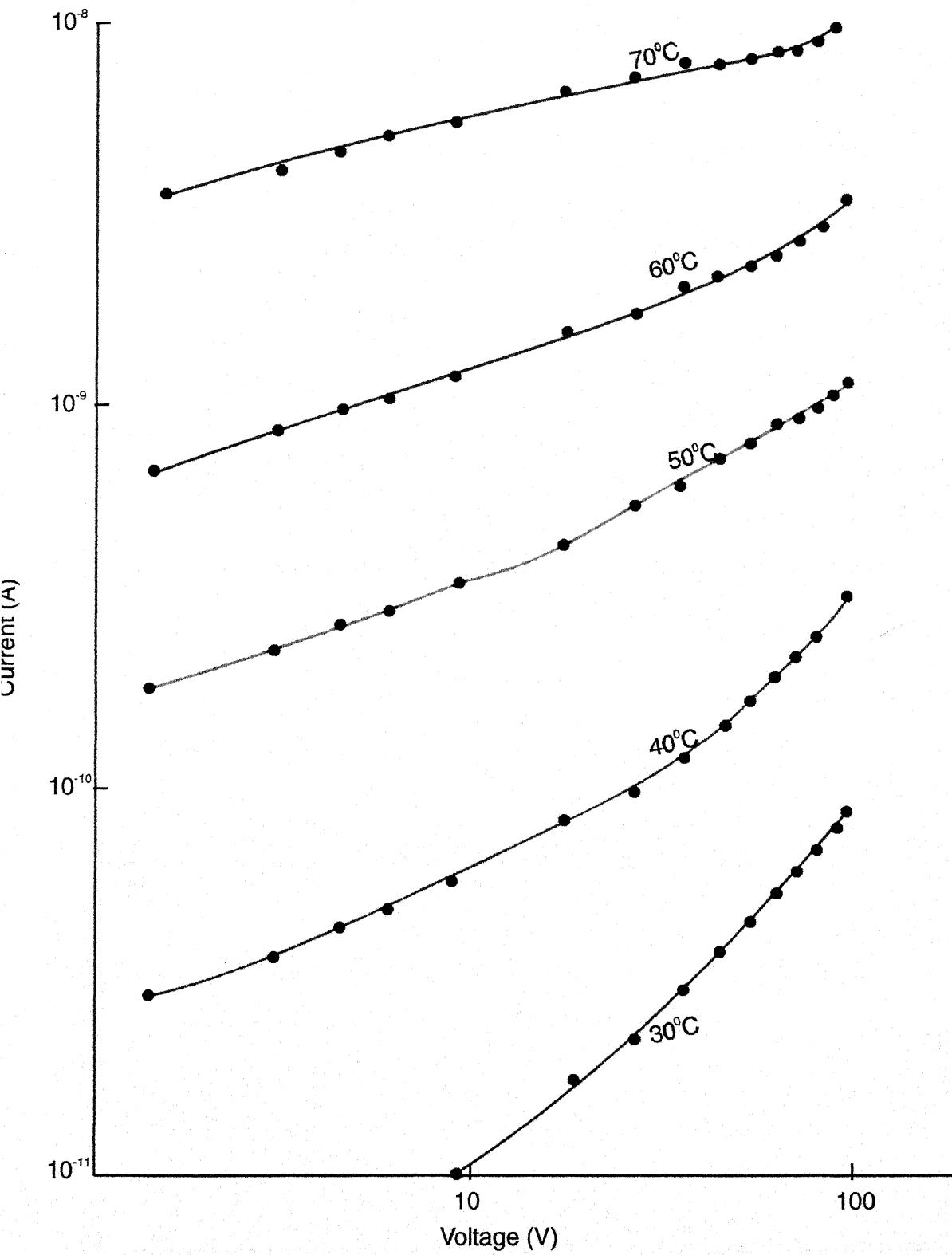
thickness. Current density at the same voltage plotted against reciprocall thickness cube of the film gave a straight line. Fig. 3.4 shows these plots for the applied voltages 1.5, 4.5, 9, 45 and 90V.

Fig. 3.5 Compares the steady state conduction currets obtained by applying a voltage in the range 3-99V at a temperature of $50^{0}C$ to the PS, I_1, I_2, I_3, I_5 and I_{10} films. They are all linear on double log scale. Currents and hence the conductivities of the doped film are greater than those of pure PS film at all the voltages applied. At a particular voltage, as the iodine concentration is increased, the current is also increaed. Slope of pure PS plot is greatest and it is decreased with the increase in iodine concentration. At a lower voltage the current differ more than at higher voltage i.e. as the voltage is increased, the difference in the currents of various samples becomes smaller and smaller.

Current voltage characteristics of I_1 at 30, 40, 50, 60 and $70^{0}C$ have been plotted in fig 3.6. Simillar plots were also obtained for other concentrotions of iodine. Slopes of these lines are seen to decrease with the increase in temperature. The

Fig. 3.7, Effect of iodine concentration on current Vs $10^3/T$ Voltage being 18V and heating rate $1^{\circ}C\ min^{-1}$ Activation energy noted on the plot
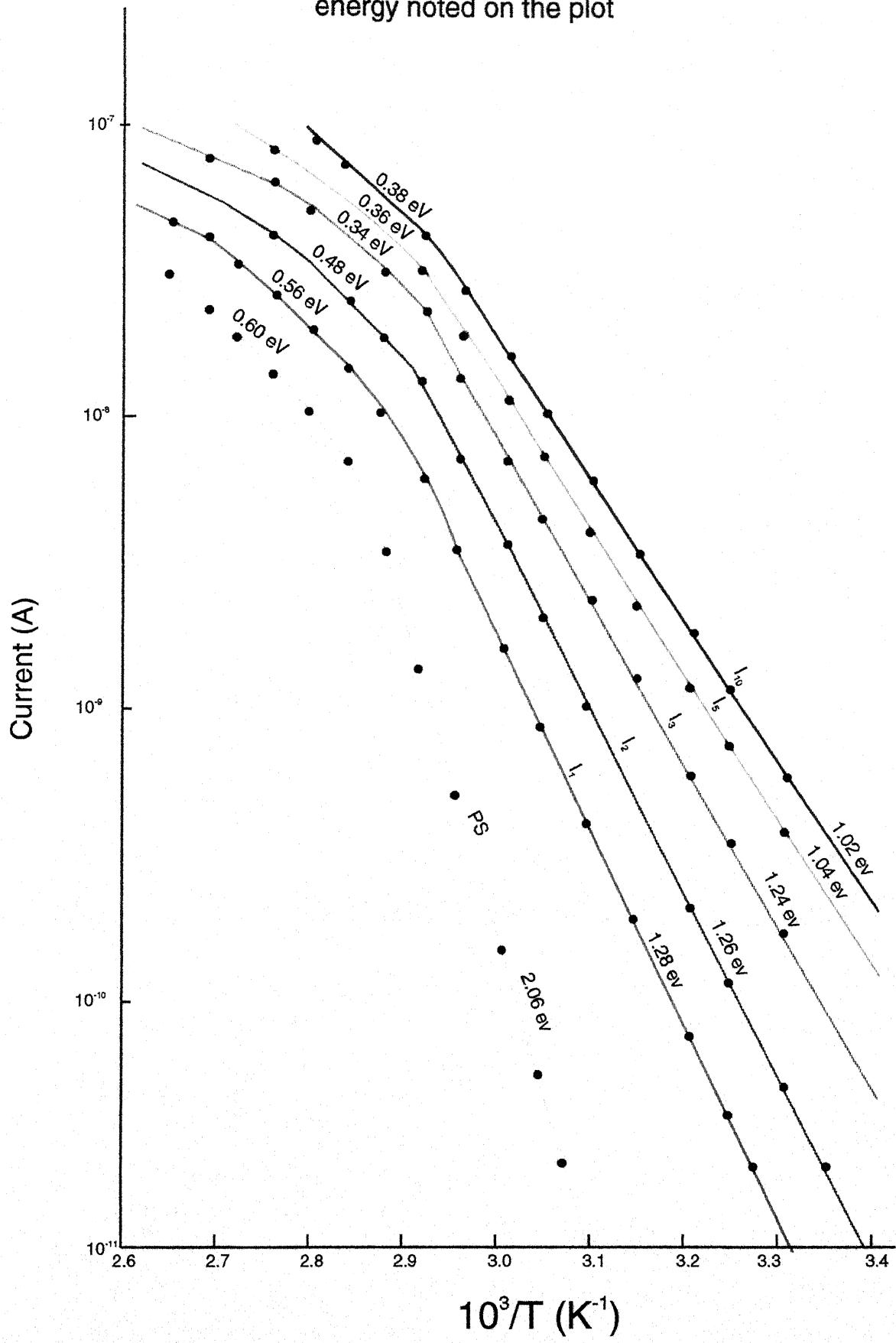
Fig. 3.8, Effect of iodine concentration on conductivity Vs $10^3/T$ Activation energy noted on the plots.
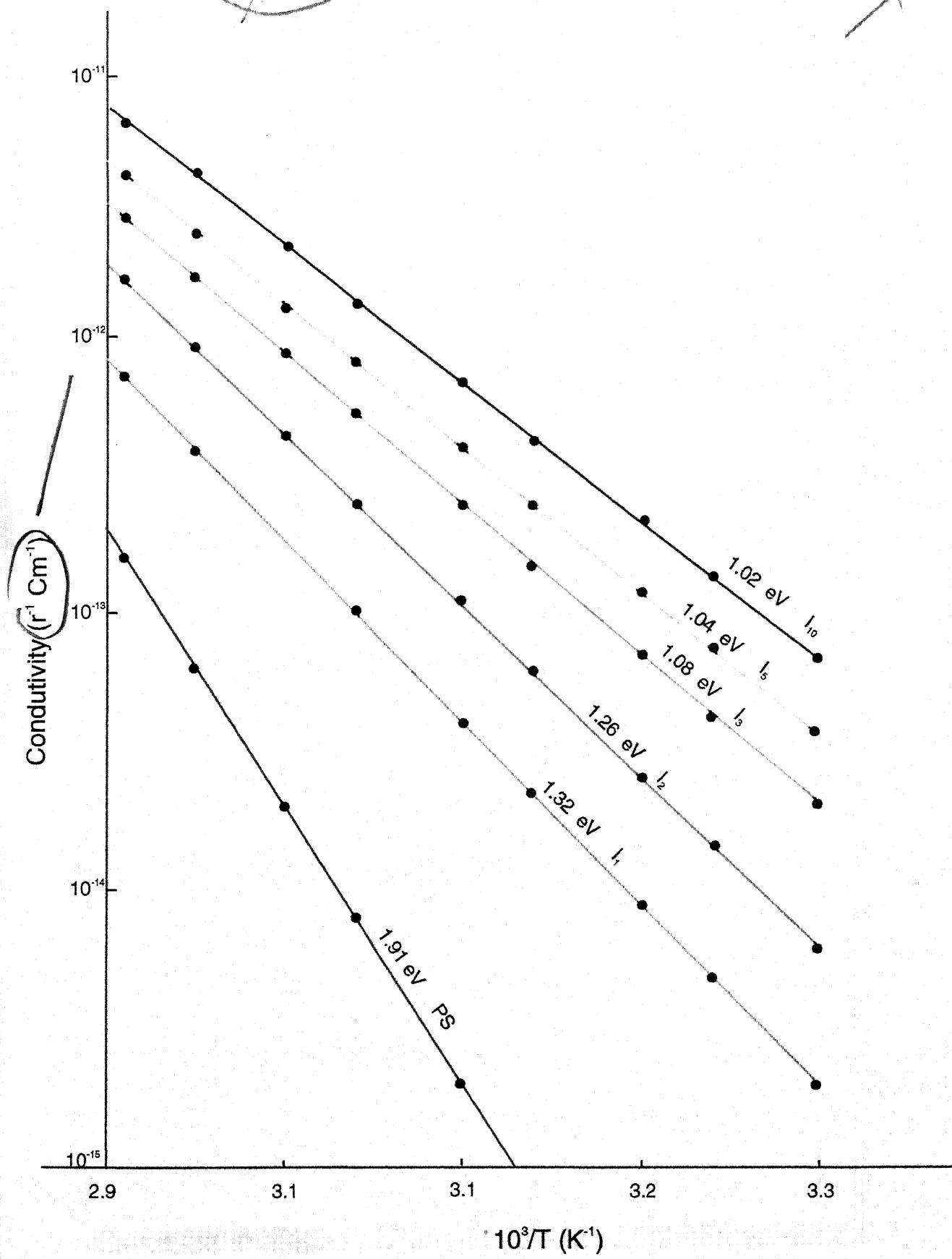
diffrence in current at various temperatures is greater at smaller voltages and is smaller at greater voltages.

The temperature variation of current in the range 30-100°C was studied by heating the film at a constant rate of 1°C min⁻¹ and applying a voltage of 18V. This is shown in fig 3.7. The conductvity was evaluated from the measured value of current. The conductivity curves (σ Vs $10^3/T$) of pure PS film and imprighated with iodine (I_1-I_{10}) are shown in fig 3.8. The conductivity of PS film increases linearly with temperature from 30°C to about 70°C beyond which a strong bend is observed. Simillar plots are seen for doped films. At all temperatures, conductivity of doped film is greater than that of pure PS. Due to increase in iodine concentration. the conductivity is further enhanced. Activation energy E was calculated from

$$\sigma = \sigma_0 \exp (E/kT) \, ... \qquad ...3.3$$

where k = Boltzmann's Constant

The value of activation energy is noted on the corresponding plot. The value of activation energy decreases due to dopping which is further decreased due to increase in iodine concentration.

3.3 Discussion.

Electronic conduction may be due to the motion of free carriers, electrons in the conduction band and holes in the valance band or alternatively to the motion of quasi-localized carriers which is otherwise described as hopping of bound carriers between localized sites (278) in the dielectric. The former process requires an activation energy in order to excite a carrier into relevant band and this energy can normally be supplied thermally or by other free carriers which have acquired a high energy in an electric field, leading to an avalanche process. The activation energy may be affected by electric field as in the case of Poole-Frenkel effect (279).

The hopping process. requires less energy than the activation into the free band and this energy may, in the limit of very high density of localized centres, tend to zero as in the case of impurity band conduction in semiconductors (280). This process is favoured in the case of heavily disordedred solids, such as amorphous and glassy dielectric films (281).

Some dielectrics show a region of linear current voltage characteristics i.e., ohmic conduction at low fields (282),

specially at elevated temperature although more often this region can not be seen at the limit of detection. It is difficult to establish conclusively whether ohmic conduction is due to ionic or electronic processes but ionic conduction would appear more likely.

In interpreting the properties of dielectric films. one frequently employs concepts taken over from the physics of crystalline media. In this way one refers to trapping levels and donor and acceptor levels at discrete energy values. One speaks of energy barriers due to ionized impurities and, in the case of Poole-Frenkel effect one employs the model of hydrogenic impurities in which the bound electron is characterized by a definite effective mass and a ground state orbit of a diameter corresponding to several interacting spacings. These concepts may be valid to a greater or lesser extent in the case of poly crystalline and micro crystalline films, although allowance may have to be made for the presence of interfacial barriers, It would be very difficult to justify their use in application to amorphous and glassy films (283). It is appropriate to recall here the salient features of the theory of amorphous conductors as it applies to dielectric

films. The general consensus of opinion is that the basic features of the band structure, such as the width of the forbidden gap, are determined primarily by the short range order i.e., by the relative disposition of the nearest neighbours in the solid. Since these dispositions are similar in amorphous and crystalline solids, the broad features are preserved on transition from crystalline to amorphous structue. The disappearance of medium and large range order does influence the detailed shape of the band structure, however, in that case it causes a considerable blurring of the edges of the conduction and valence bands, and gives rise to a distribution of deep localized levels in the forbidden gap.

In a crystalline solid, there exists a clear distinction between the propagating bands-conduction, valance and forbidden. In the former the carrier propagate freely except for collisions on thermal vibrations and other lattice imperfections which determine a mean free path which is greater, usually considerably greater than the lattice spacing. In the forbidden gap the energy levels that may exist due to imperfections are strictlly localized and an electron has to be exited from one of these levels to the conduction band before being able to move on. Special case arises when the localized levels are spaced so closely that their wave

functions overlap and give rise to the formation of the so called impurity band, leading to metallic properties with zero activation energy. Alternatively, the spacing may not be as close as is necessary for the formation of impurity band, but sufficient for phonon assisted tunnelling between neighbouring centres, the so called hopping conduction. Hopping is characterized by an activation energy which is only a fraction of the normal ionisation energy of the carrier from the centre into the band is often accompanied by a rather complicated frequency dependence.

The significance of blurred band edges is that there is no sharp distinction between the propagating and forbidden gap but instead partly localized levels are formed leading to a conduction by a process intermediate between impurity band and hopping conduction in which the propagation of the carriers is characterized by a small mobility. The deeper the levels, the more localized their character, until the deep tail states may be considered as proper trapping sites, unlike traps in crystalline materials, However, these deep states would not possess any clearly defined activation energy.

Poole-Frenkel mechanism is frequently invoked in

the interpretation of electric currentin dielectic films at reasonably high electric fields. The physical basis of Poole-Frenkel mechanism is analogous to the Schottky emission.

O' Dwyer (284) in a theoritical paper considers a detailed electronic model of a dielectric with traps with Schottky emission from an injecting electrode and with Fowler-Nordheim correction for tunnelling through the top of the barrier at high fields. In a recent review of Poole-Frenkel mechanism Simmons (285) pointed out that experimental data apparently favouring the Schottky mechanism can be more compatible with Poole-Frenkel mechanism if it is postulated that shallow neutral traps are present in the dielectric togeter with deep lying donors. Franks and Simmons (286) consider further the effect of space charge on Poole-Frenkel process.

A consequence of a phenomenon of carrier injection is the formation of space charge cloud (287, 288) of carriers in the vicinity of contacts. Mutual repulsion between the individual carriers limits the total injected charge in the film and the resulting current is said to be space charge limited. Trapping sites reduce the magnitude of current. The mobile charge carriers are

continually interacting with the lattice. A thermodynamical equilibrium is maintained between the space charge and lattice so that there is a special relationship between the electric field and the drift velocity of the carriers. The trapping sites accentuate this difference even further. Holes or electrons can be injected according to the choice of electrode material (289). This then brings in the added complication of recombination.

3.3 (a) Transient Current:

When a DC field is applied to a finite thickness of a dielectric sandwiched between two parallel electrodes, there is besides the rapidly charging current and steady state conduction current, a long term slowly decaying current. Similarly, on removal of the voltage and the electrodes short-circuited, the fast component of the current is followed by a long term slowly decaying current. This long term current is known as the anamolous current or absorption current (290). Provided the principle of superposition holds, the behaviour of change in current with time for the charging and discharging events are equivalent and their numerical analysis are identical. The discharge current manifests itself in a familiar absorption of the charging

experiment. Dielectric relaxations which occur in the frequency range 0.1 Hz are normally studied by their contributions to the current decay of a charged dielectric on discharge (291).

Das Gupta and Joyner (290) reported absorption current in polyethylene terephthalete and polypropylene by varying field, temperature, time, electrode material and thickness and identified the mechanism from the possibilities electrode polarization, dipole orientation, charge storage leading to trapped space charge effect, tunnelling of charge carriers from the electrodes and hopping of charge carriers through locallized states. The behaviour of absorption current in iodine doped PS is observed to be similar to that of polypropylene. A sudden increase in voltage causes the current to transiently increase to high values. In a matter of minutes, the current subsides to a much smaller stationary value. The interpretation is that the sudden increase in voltage forced a corresponding increase of charge in the conduction band. In the course of minuts, most of this free charge settles into traps and one observes the rapid decay of current. The time required for the transient current to subside is a direct measure of the capture cross-section of traps for free

carriers.

The transient current J versus time t on a double log scale yields a straight line (fig 3.1) showing that the decaying current obeys the usual t^{-b} law (b; an eponenet ; $(0 < b < 1)$ before reaching a steady state.

The absorption current shows a marked increase with temperature. The observed magnitude of b in the temperature range and the absence of any thickness dependence and any significant electrode material effect (not Shown) rule out tunnelling, electrode polarization and charge injection forming trapped space charge as possible mechanisms for absorption currents. The observed behaviour of absorption current in the temperature range may be explained either by the mechanism of dipolar relaxation in the bulk with the wide distribution of relaxation times or by a charge carrier hopping process through localized states. A relaxation of dipoles may also be ruled out as a relevant mechanism because the absorption current was not found to be inversely proportional to the sample thickness (292).

3.3 (b) Effect of Electrode Material:

Charge transfer from metal depends on electron

levels in which the carriers shift freely under the influence of field. The energy on this level (293) may be given by

$$E_b = E_g = (I_g - P^+) - (A_c + P^-) = I_c - A_c$$

Where Ig is ionisation energy, Ac electron affinity, P^+ and P^- polarization energies and Ic ionisation energy of a molecule of the material, E_b corresponds to energy gap Eg. In case of PS E_b = Eg = 4 - 5 eV, from this data intrinsic generation of free carriers resulting from Boltzmann's factor is negligible at temperatures below polymer decomposition. It gives more emphasis to the importance of metal-electrode contact which is the origin of carriers responsiable for conduction.

The contact is said to be ideal if the distance between metal and dielectric is 10A°. If no excess ions or other energy states appear in the dielectric, the fermilevel is midway between conduction and valence band. The fermilevel is away from the vacuum level by ϕ (ϕ corresponds to work function of electron detached from the metal). When the metal comes into the contact with the dielectic, there is a tendency towards equalization of levels at the point of contact. If the fermi level is higher in the dielectric than in the metal, then electrons are transferred to the

metal and in this way a levelling of potentials takes place. In the case of organic compounds, there are no excess charges even if there are defects, they are deep and therefore can not go ionization under the influence of thermal energy, the same applies to impurities from the other organic molecules. Electrostatic equilibrium is established only due to transfer of carriers from metal. Electron over comes the potential barrier (designated by χ)

$$\chi^- = \phi - A_c \qquad\qquad ...3.4$$

while holes must overcome the potential barrier

$$\chi^+ = Ic - \phi \qquad\qquad ...3.5$$

Where ϕ is the metal work function. In this way emission current arises as described by Richardson's equation:

$$J = AT^2 \exp(-\chi/kT) \qquad\qquad ....3.6$$

Where J is the current density, A is a constant, T is the absolute temperature and k is Boltzmann's constant.

In the light of above discussion, J-V$^{1/2}$ plot (fig 3.2) may be interpreted in terms of Richardson-Schottky (RS) field assisted thermionic injection of carriers from metal electrodes.

The RS mechanism has also been suggested in other studies on polyethylene terephthalate, polytetrafluore thylene and poly N-vinyl carbazole (294, 295). The simple RS theory does not give a good fit to the experimental data and various explanations have been advanced to explain this. Schug etal (296) have concluded that the electric field in the RS effect is determined by the trapped space charge moderated by Poole-Frenkel effect (285). Taylor and Lewis (297) have assumed a more generalised form of the potential barrier rather than the Coulombic barrier usually emplooyed in treatments of the RS effect. They obtained consistent agreement with experimental results in studies on polyethylene and polyethylene terephthalate and concluded that the potential barrier chosen referred to the cathode-dielectric interface and is probably deteremined by a space-charge layer in the dielectric. It has been suggested that such space-charge layers are charged up by the absorption current (298, 299). The classical RS effect predicts a current-voltage relationship of the form :

$$J = AT^2 \exp(-\chi/kt) \exp(\beta V^{1/2}) \qquad ...3.7$$

$$\text{with } \beta = e/kT \, (e/4 \pi \varepsilon \varepsilon_0 d)^{1/2} \qquad ...3.8$$

Where, d is the film thickness, ε is the dielectric constant, ε_0 is

the permittivity of free space and e is the electronic charge. For zero field, this equation reduces to the previous one and the current density depends on the potential barrier at a constant temperature. Zero field current density does not vary with metal work function.

3.3 (C) Thickness Dependence:-

A consequence of the phenomenon of carrier injection is the formation of a space charge due to their trapping in different trapping sites. Mutual repulsion between the individual carriers limits the total charge injected in the sample and the resulting current is said to be space charge limited current (SCLC). Certain requirements are to be fulfilled for such a flow of injected charge to take place and be detected. The first stringent condition is that the electrodes furnish ohmic contacts to the solid. Secondly the insulator should be relatively free from trapping defects and the contribution of thermally generated carriers be small.

The complete mathematical analysis of time independent SCLC in solids is so complex that no explicit expressions have yet been obtained relating the current and

voltage. Mott and Gurney (300) were the first to emphasize the importance of an injecting contact between a metal and an insulator and they provided an approximate expression relating the current, voltage and thickness in a trap free insulator. A slight modification of their theory results in the following relationship between current, voltage and thickness for a SCLC.

$$J = \frac{9\theta\epsilon\mu v^2}{8d^3}.$$

... 3.9

In this equation μ is the mobility of carriers, ϵ and d are the permittivity and thickness of the sample and θ is the fraction of total carriers (all electrons above the Fermilevel) which are free.

The above equation is a special case of the general scaling law for bulk space currents in a homogeneous medium which is :

$$J \propto d \, (V/d^2)^n$$

... 3.10

Where n is a constant which need not necessarily be an integer. For example in the trap free insulater case, n=2 , while for double injection, n=3 and for recombinative space-charge

injection, n = 1/2 (301, 302).

The introduction of deep trapping centres in the solid can result in a higher power dependence of current on voltage than the square law relation. It is evident that as more and more electrons are injected into a solid, the traps will gradually get filled up and eventually no more injected electrons are trapped. The first approximate treatment of this problem was by Lampert (262) who considered a model containing a set of defect states at a single discrete energy level.

It is of importance to be able to distinguish between non-ohmic behaviour due to space charge and that arising from other physical process. The obvious method is to investigate the dependence on thickness of a set of current-voltage curves (3.3). Thin films give more current. It is the evidence of space charge accumulation. Pulfrey et al.(303) consider electronic conduction and space charge in amorphous insulating films and conclude that at small thicknesses Schottky law is more probable while at large thickness the Poole-Frenkel law is expected. Linearity of current density versus reciprocal thickness cube plots (fig. 3.4) is the ample proof of SCLC in iodine doped PS-matrix.

3.3 (d) Current Voltage Characteristics :

Current-voltage characteristics (fig. 3.5 and 3.6) are linear. When the charge carriers are supplied from the electrode and all of them are transported,Ohmic law holds and the current is proportional to the voltage. The current in the case is limited by the electrode. When the electric field is low, the mobility of the carriers or the presence of traps can limit the current observed in the system. In the absence of traps only mobility limits the current and one has a super linear J-V curves (304, 305)

The plots of fig. 3.6 have been replotted in J-V½ form in fig 3.9. The plots are seen to be linear. This is naturally taken as evidence of either Schottky or Poole-Frenkel mechanism. The theoretical and experimental values of constants in Schottky and Poole-Frenkel equations show marked departures. This complicates the interpretation in terms of either of the simple models because a temperatue dependence is not provided in both the Schottky and Poole-Frenkel mechanisms.

Scher and Montorll (278) recently advanced the phenomenolgical relationship for hopping conduction in which the voltage and temperature dependence of the mobility μ is described

Fig. 3.9. Replots of fig 3.6 in J-V$^{1/2}$ form.
Temperature Noted on plot

7.4×10^{-8} A

1190 V

Current (A)

70° C

60° C

50° C

40° C

30° C

10^3/T (K^{-1})
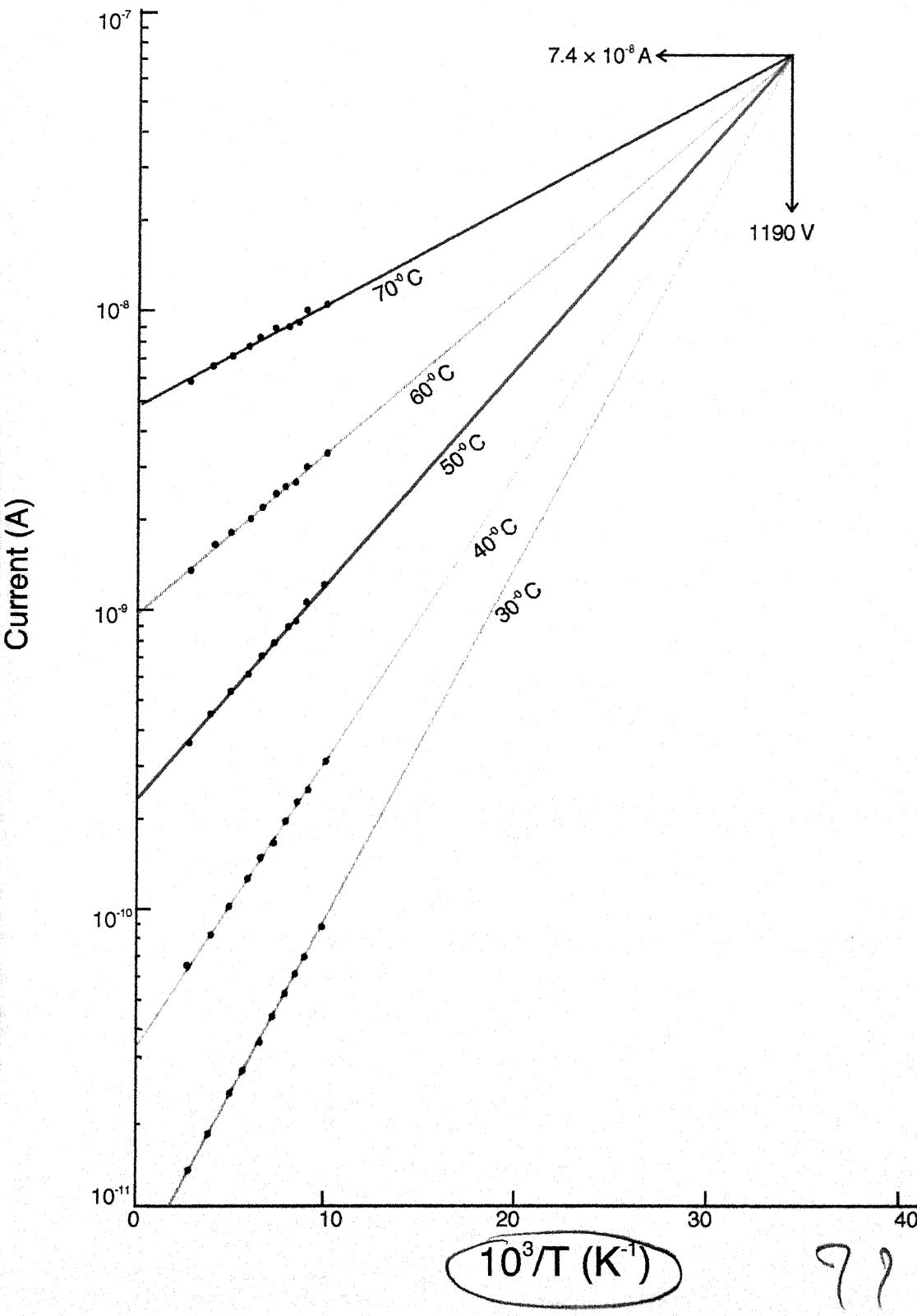
Fig. 3.10. Replots of fig 3.6 in J-10$^{1/2}$/T form Voltage Noted on the plot
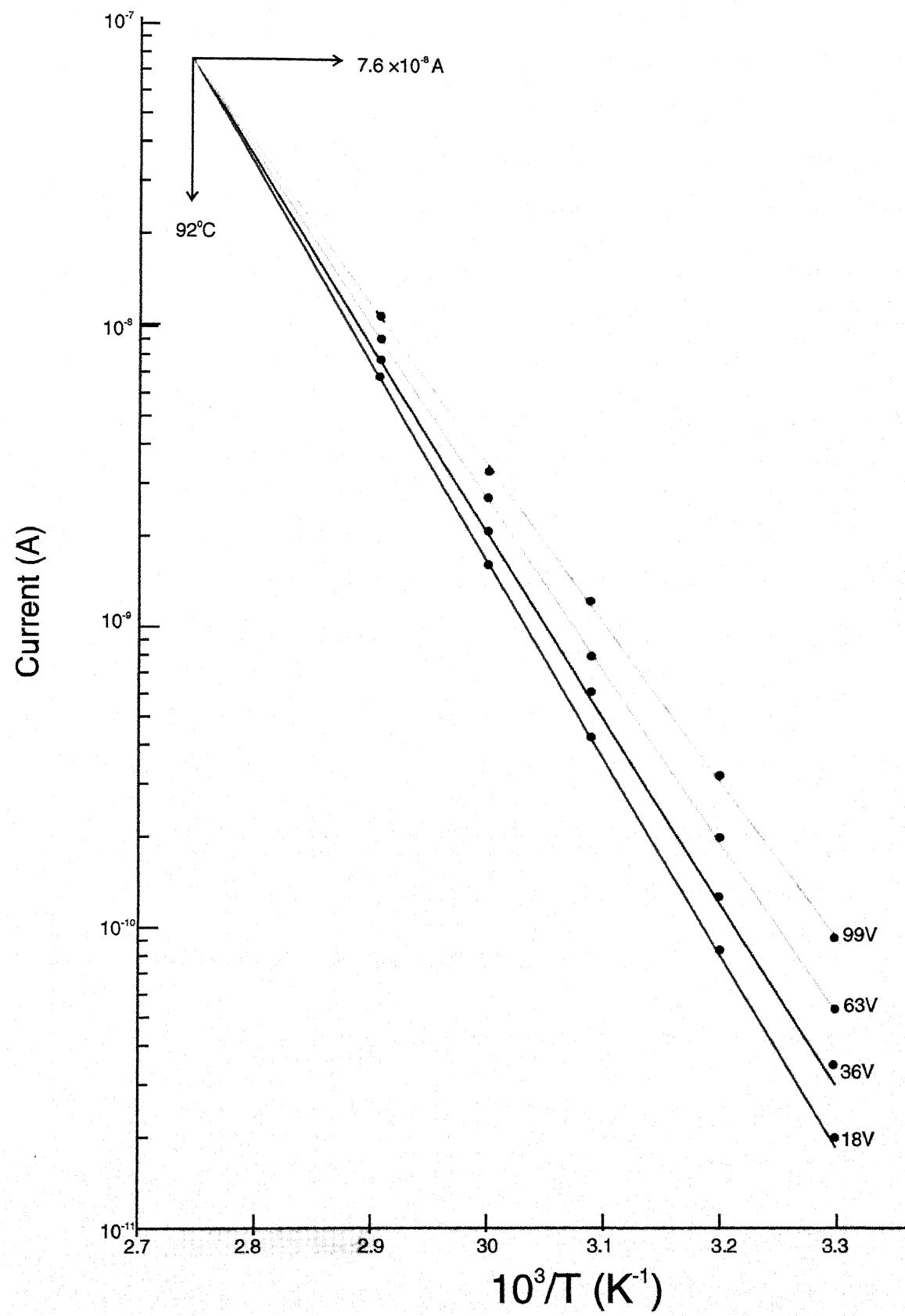
by the following equation

$$\mu = \mu_0 \exp (a/k) (V^n - V_0^n) (1/T - 1/T_0) \qquad ....3.11$$

Where μ_0 is pre-exponential factor, a, V_0 and T_0 are parameters and n approximates to 1/2. In fig. 3.9 the square root voltage dependence of current is shown for temperatures 30, 40, 50 , 60 and 70°C. The straight lines when extended have a comman intercept. The values of current and voltage at the intercept are found to be 7.4×10^{-8} A and 1190 V respectively. The same results are reploted in fig. 3.10 as a function of $10^3/T$ for voltages 18,36, 63 and 99 V. The straight lines when extended have a comman intercept. The values of current temperature at the intercept are found to be 7.6×10^{-8} A and 92°C respectively. The values of current obtained from the two intercepts are in very good agreement. Therefore the current and hence, the mobility is described by the above equation in iodine doped PS films.

3.3 (e) Effect of dopant concentration on temperature dependence of conductivity-

The interpretation of the temperature dependence of conductivity in polymers is far from consistent. Some hypothesis have postulated that conductivity above and below the inflection

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is ionic and electronic in nature respectively and yet other are based on the analogy with some intrisic conduction exists above inflection and impurity conductivity below inflection. Shishkin and Vershinina (306) and Warfield and Petree (307) connect the inflection with glass transition of the polymer. They explain the inflection at glass transition by change in environmental condition for ion mobility at the transition from the glassy state into a highly elastic one. Herwig and Jenckel (308) and Raddish (309) suppose that the inflection appears as a result of the superposition of polarization effects on the conductivity process at temperature below the glass transition temperature, at which the relaxation time becomes long. Adamec and Mateova (310) concluded that the inflection on J (T) curve does not necessarily correspond to the glass transition temperature of the polymer, even though the inherent conductivity becomes a predominating component in the vicinity of glass transition.

High activation (fig. 3.6) arises from intrinsic conduction. The difference in activation energies is due to higher dissociation energy to form the carrieres for intrinsic conduction. Similar results of doping have been reported for poly vinyl fluoride (311) and polystyrene (180). The conductivity is

enhanced considerably, which may be associated with the increase in mobility due to doping. The strong concentration dependence of conductivity of the polymer helps to interpret that transport in iodine doped PS films occurs via a hopping process among sites associated with the dopant molecule. A rather detailed theoritical background exists for hopping transport with a discrete activation energy. Theoritical refinements are in progress to include distrigution of hopping energies and to describe alternative transport mechanisms such as multiple trapping and trap-controlled hopping (312-316), although these extensions of the theoritical concept will narrow the range of possible interpretation would require the experimental modifications of materials parameters specific to the proposed transport model, such as the densities of hopping or trapping sites. In this respect, the concept of doping of organic polymers is extermely powerful.

3.4   Conclusions:

The above discussion on electrical conduction in iodine doped PS films enable to draw the following conclusions.

1.   The transient current decays according to t-b law before reaching a steady state. The observed magnitude of b and the

lack of thickness and electrode material dependence of transient current indicate carrier hopping process.

2. Electrode effect on current-voltage characteristics of the films indicates the Schottky thermionic emission of charge carriers.

3. Thickness variation on current voltage curve of doped PS reveals space charge build-up.

4. In low field regime Ohm's law seems to be valid in iodine doped PS films.

5. At high field values, the linearity of current with square root of volt age indicated Schottky or Poole-Frenkel mechanism. But the poole-Frenkel mechanism is more logical because comparatively thick $(20\mu$ m) films have been used in the investigation.

6. The experimental value of Poole-Frenkel coefficient is calculated to be very low in comparison to the theoritical value. This complicates the interpretation of current-voltage characteristics in terms of Poole-Frenkel mechanism and shows a temperature dependence which is not provided in the simple model for Poole-Frenkel mechanism.

7. The value of current for iodine doped films determined from the common intercept of current versus square root voltage at various temperatures agrees well with the value determined from the common intercept of current versus $10^3/T$ at various voltages. This shows that the field and temperature dependence of mobility in the films can be described adequately according the equation.

$$\mu = \mu_0 \exp (a/k) (V^n - V_0^n) (1/T - 1/T_0)$$

The above equation is the phenomenological relationship for hopping conduction as described by Scher and Montroll.

8. Temperature dependence of conductivity of pure and iodine incorporated films reveals that doping of the PS matrix with iodine enhances the conductivity of the polymer. The increase in conductivity is due to the increase in mobility of charge carriers due to impregnation of the matrix with iodine.

9. Iodine is a strong electron acceptor impurity. It forms charge transfer complexes (CTC) and so the conductivity is enhanced.

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Chapter-4
Dielectric properties

DIELECTRIC PROPERTIES

4.1 Introduction

The dielectric behaviour of polymeric films is of direct interest to both the basic studies of electrical conduction through such films and their applications in capacitors for micro-electronics. To obtain high values of capacitance, the dielectric constant should be high and the thickness be small. Due to the difficulty of obtaining structurally continuous and stable ultra thin films, capacitor applications are generally limited to thick films.

The evaluation of dielectric properties of insulator films (317-321) is carried out by measuring simultaneously the capacitance and the dissipation factor over a wide range of frequencies and temperatures. As all the other electrical parameters of dielectrics, the permittivity depends on the changeably external factors such as the frequency of voltage application, temperature, pressure, humidity etc. In a number of cases these dependences are of great practical importance.

Recently dielectric properties of several polymers (322-341) polar and non-polar have been investigated. Some general relations between dielectric properties have been

discussed, distinguishing between resonance phenomena that commonly occur in the optical region and relaxation phenomena which occur in polymers at the lower frequency regions. It has been shown how the real and imaginary parts of the complex constant depends primarily on the density, but little is known regarding the nature of the dielectric loss. Attention has also been paid to polar polymers. After some preliminary remarks on the nature of dielectric dispersions, some phenomenological notions of dielectric dispersions have been considered, Attempts have been made to relate theory and practice. The topics, such as phase transitions, anisotropy and inhomogeneity have been dealt with. Dielectric relaxations in polyvinyladene fluoride were studied by Sasabe et at (324) They observed three distinct absorption peaks (α, β, γ) in the frequency range from 0,1 to 300Hz in the temperature range -66 to 100°C. The γ absorption is related to molecular motion in the crystalline region. The β absorption can be interpreted as due to the micro-Brownian motion of the amorphous main chains. The α absorption is attributed to local oscillations of the frozen main chains, Kakutani and Ashina (325) studied low- temperature absorption of polyvinyl chloride and concluded that. the γ and β processes are the result of molecular

motion in crystalline and amorphous regions of the polymer respectively. Low temperature dielectric relaxation in polyethlene and related hydrocarbon polymers was investigated by Phillips (342). He uses a simple quantum mechanical model of relaxation process to explain the experimental results. According to this process, a particle in a double potential well tunnels from one well to the other with emission or absorption of a phonon, Results of Kawamura et at (322) on dielectric properties of co-polymer of methyl-methacrylate with n-bityl methacrylate lead to the fllowing conclusions.

1 The loss peak temperature attributed to side chain relaxation varies with the comonomer ratio when the comonomer does not have a methyl group but remains almost unchanged for comonomer having methyl group.

2. In both cases, The β-peak hieght decrease with increasing ratio of comonomer. It is suggested on the basis of the above facts that the moving unit in the side chain relaxation consists of single side chain with a segment of the backbone chain and that the change in mobility of the side chain upon copolymerization results from the distortion of the helical structrue of the backbone chain due to random distribution

of methyl groups.

Though there is a wide literature available on dielectric properties of polymers, yet a few reports (343-345) exist on impurity doped polymers. Kokasi and Ieda (343) have doped high and low density polythylene. One of them has the loss maximum dependent on the amount of the impurity and is related to the relaxation of a dipole orientation of the impurity. Another shows an odd behavior named retrogressing phenomenon near the melting point of polyethylene and can not be detected in the amorphous polystyrene doped with the same impurity. An interfacial polarization is proposed assuming a model which is justified semi-quantitatively. The retrogressing phenomenon is explained by the change of the layer thickness that affects the dielectric relaxation time of the model. Kulshretha and Srivastava (344) doped polystyrene with chloranil and Srivastava et al (345) with copperphthalocyanine and observed interfacial polarization in the measurement of dielectric losses of the polymer.

Less has been reported on dielectric properties of doped PS (346) and it seems to carry out further investigations to understand the dielectric behaviour of the doped polymer. This

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FIG 4.1 Capacitance Vs frequency at different temperatures for PS and I, it also shows effect of iodine Concentration at 30°C
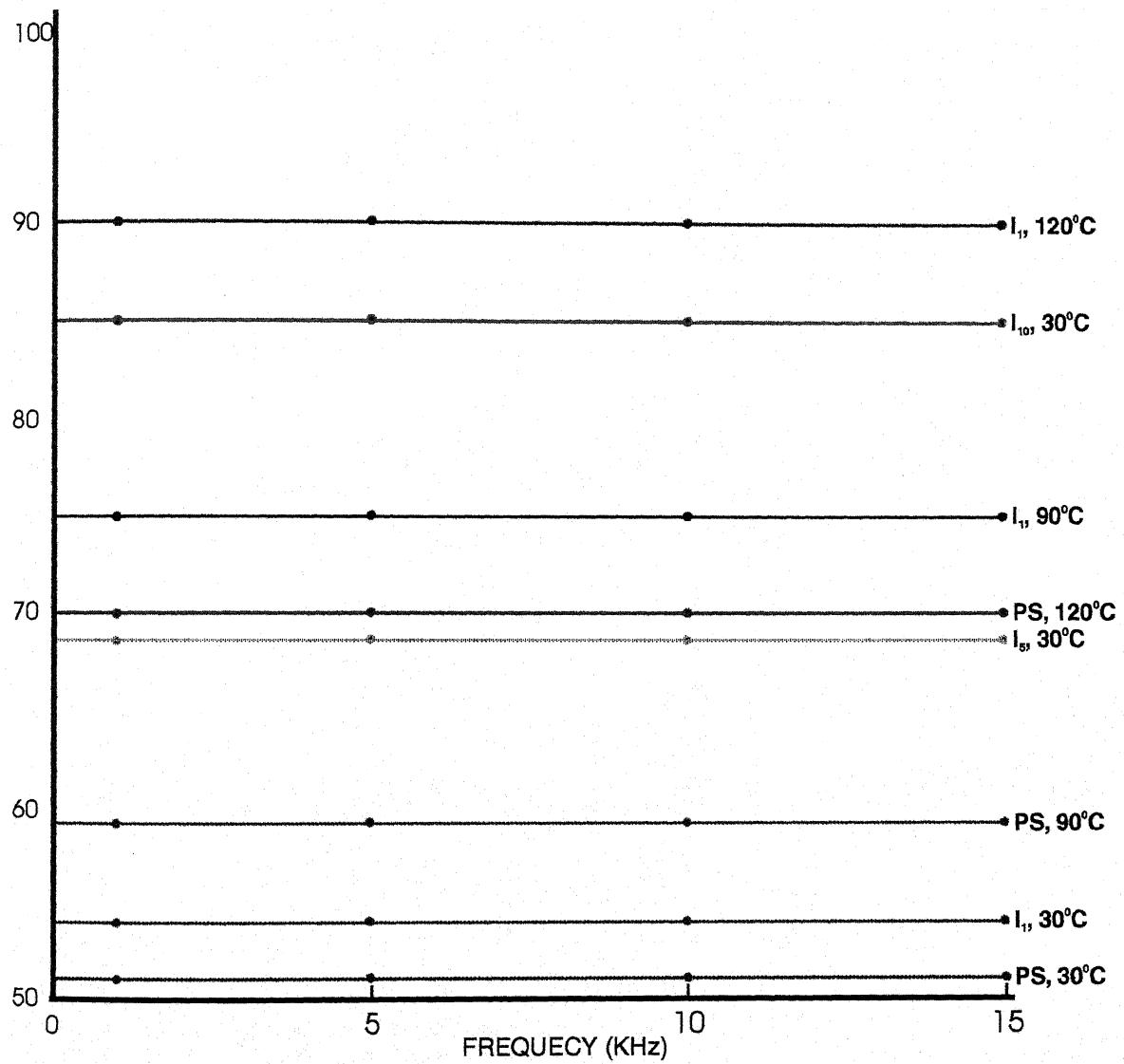
Fig. 4.2 Capacitance Vs Temperature for PS & For I_1, I_2, I_3
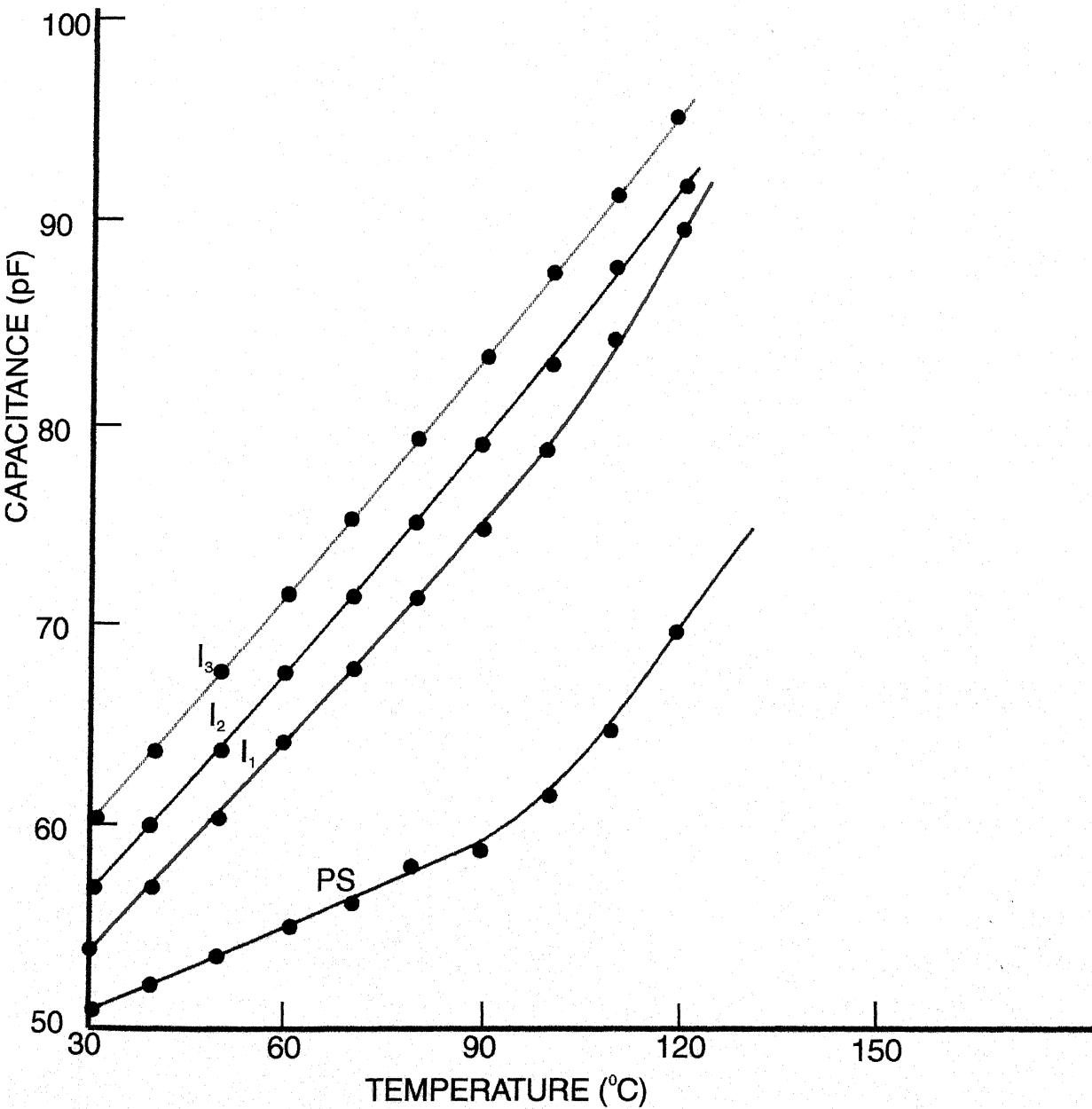
FIG 4.3 Capacitance Vs Iodine Concentration of various Temperatures
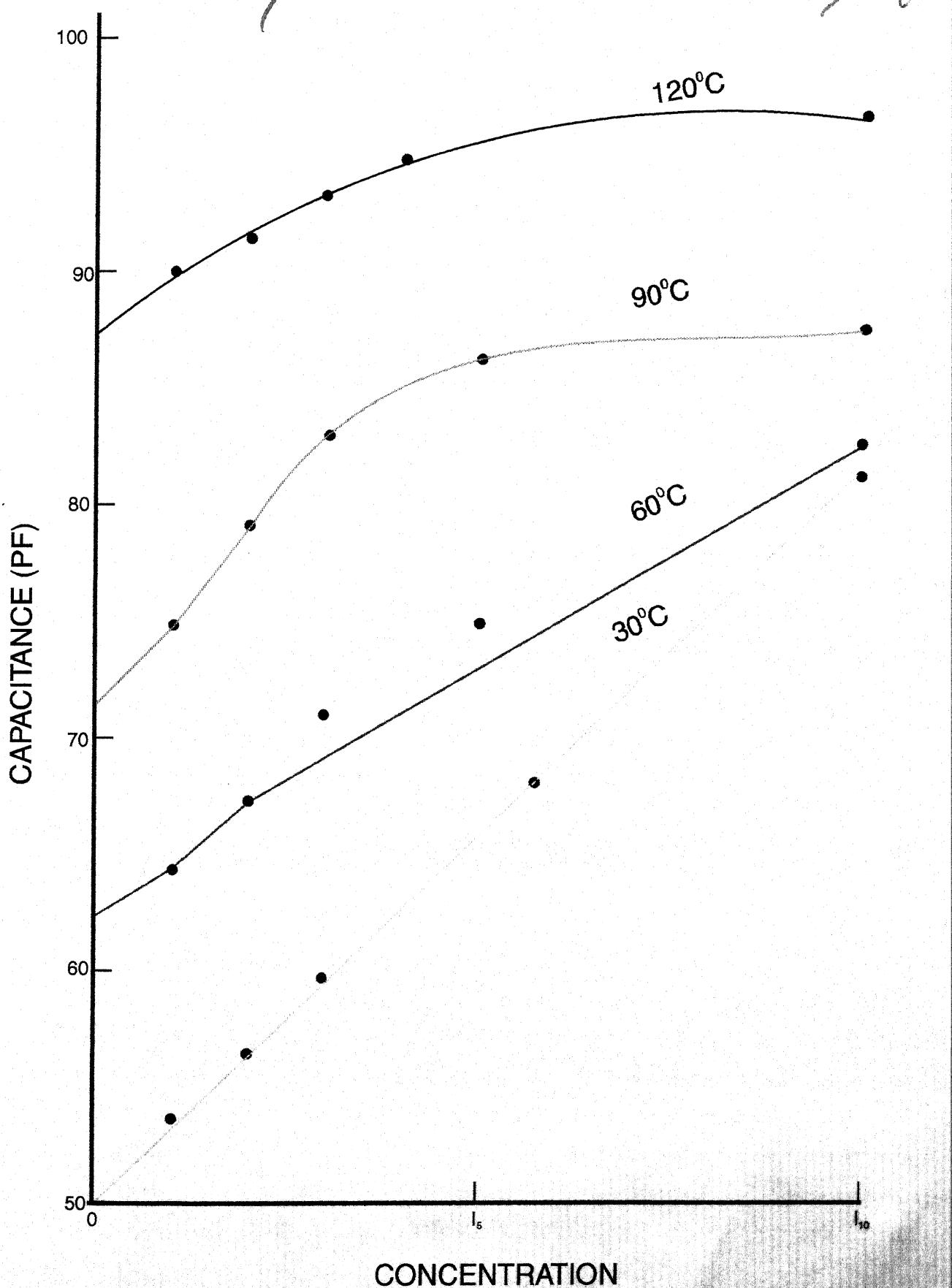
Fig. 4.4 Loss tangent Vs Temperature at various frequencies depicting for PS & For I₁, & I₃

I_1, 300 Hz

PS, 300 Hz

I_1, 500 Hz

I_3, 2 K Hz

I_1, 2 K Hz

PS, 2 K Hz

Loss Tangent
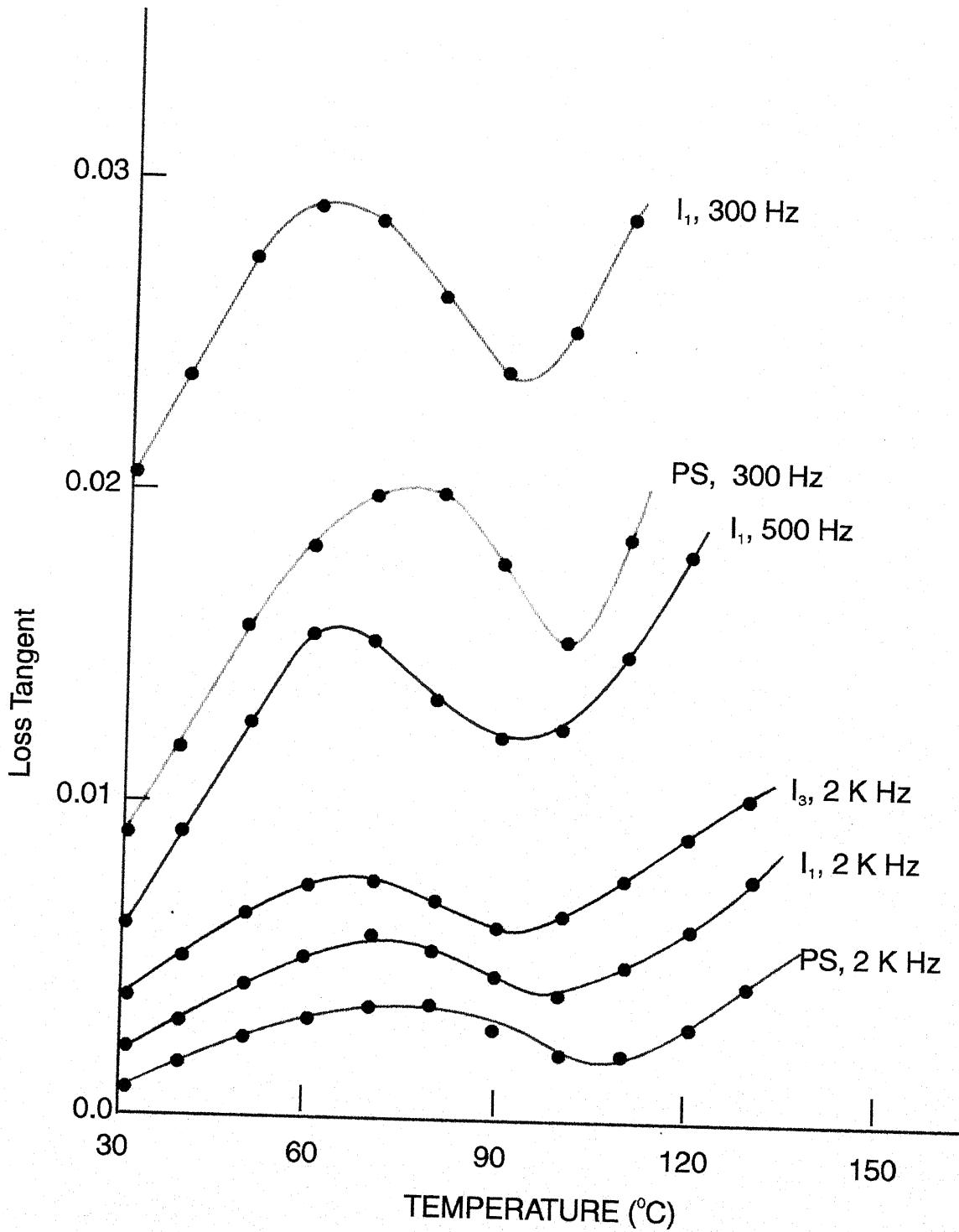
TEMPERATURE (°C)

chapter reports on capacitance and dielectric loss factor of iodine doped PS films as a function of temperature and frequency in audio frequency range.

4.2 Results

Dieletric properties of polymers are investigated by measuring simultaneously the capacitance and the losses at regularly varying temperature and frequency. Capacitance as a function of frequency for PS and I_1 at 30, 90 and 120^{0}C is shown in fig 4.1. Fig. 4.2 also shows the effect of iodine concentration at 30^{0}C.There is no variation in capacitance with the frequency in the range (0-15 KHz). Due to increase in temperature capacitance increase. Similar results were also found for other concentrations of iodine incorporation. Due to doping capacitance is increased which is further increased due to increase in iodine loading. Fig.4.3 exhibits capacitance versus iodine concentration at 30, 60, 90 and 120^{0}C temperatures. Capacitance increases with the increase in iodine concentration as well as with the increase in temperature. Fig 4.4 illustrates the effect of concentration of iodine incorporation in PS on tanδ (loss tangent) versus temperature at 2kHz. For the sake of comparision the plot for pure

PS film has also been included in fig 4.4. For PS a loss maxima at 85^0C is observed. Due to doping , this loss maxima is shifted to a lower temperature. For concentrations I_1 and I_3 the loss maxima occurs at 78, and 70^0C repectivly. Loss is increased due to doping which is further increased due to increase in dopant concentration. It is also clear form fig 4.4 that due to decreas in frequency dieletric loss is increased and the loss maxima shifts to a lower temperature. Fig 4.5 shows tanδ versus iodine concentration at 30^0C and at a frequency of 2kHz. the plot is a straight line. In fig. 4.6 $\log f_{max}$ versue 10^3/T has been plotted for PS and I_1. The plots are straight lines. The value of activation energy is calculated to be 0.72eV for pure PS and 1.12eV for doped PS. Due to doping activation energy is increased. Due to increase in iodine concentration there was no regular and significant difference in activation energy.

4.3 Discussion :

Permittivity is the basic parameter of a dielectric describing its properties from the view point of the process of its polarization or propagation of electromagnetic waves in it, or more generally from the point of view of the processes of its interaction with an electric field. Permittivity is a macroscopic

parameter of a dielectric which reflects the properties of a given substance in a sufficiently large volume but not the properties of the separate atoms and molecules in the substance. There are three well know types of polarization: Electronic, ionic and dipole polarization.

Electronic polarization is the displacement of electrons with respect to the atomic nucleus, to be more precise the displacement under the action of an external field of the orbits in which negatively charge electrons move around a positively charged nucleus. This type of polarization occurs in all atoms or ions and can be observed in all dielectric irrespective of whether other types of polarization are displayed in the dielectrics. One specific feature of electronic polarization is the fact that when an extenal field is superposed, this type of polarization occurs in a very short interval of time (of the order of 10^{-15} seconds) i.e. the time of the period of oscillation of ultraviolet rays.

Ionic polarization is the mutal displacement of ions forming heteropolar (ionic) molecules. A shorter time is required for the process of ionic polarization to set in, but is longer than that of electronic polarization, i.e. 10^{-13}- 10^{-12} seconds. On the

whole the process of electronic and ionic polarization have much in common. Both phenomena may be regarded as the varieties of polarization caused by deformation which is a displacement of charges with respect to each other in the direction of the field. Apart from a very high velocity mentioned above with which the state of polarization sets in, it is important to bear in mind that the process of deformational polarization is practically unaffected by the temperature of the dielectric and is not connected with an irreversible dissipation of energy. The electric energy required to polarize a molecule is completely returned to the energy source after the voltage is removed. For this reason deformational polarization does not enter any dielectric losses.

Polar dielectrics (347-350) exhibit a tendency towards dipole or orientational polarization. The essence of this kind of polarization can be reduced in a simplified manner, as has been first suggested by Debye, to the rotation of the molecules of a polar dielectric having a constant dipole moment in the direction of field. If orientational polarization is considered more strictly, it must be understood as the introduction by an electric field of certain orederliness in the position of polar molecules being in uninterrupted chaotic 'thermal' motion, and not as a

direct rotation of polar molecules under the action of a field. For this reason, dipole polarization is connected by its nature with the thermal motion of molecules, and temperature must exert an appreciable effect on the phenomenon of dipole polarization.

After a dielectric is energized, the process of establishing a dipole polarization requires a relatively long time as compared with practically almost inertialess phenomenon of deformational polarization. More or less time is needed in any individual case. As distinct from defrormational polarization, dipole polarization and also other kinds of relaxation polarization dissipate electric energy which tansforms into heat in a dielectrict i.e. this energy causes dielectric losses.

In polymers dielectric loss behaviour may be attributed to the deformationof polymer chains (351-353). The molecular flexibility of chains is responsible for this characteristic property of the polymers. The other important mechanism for the dielectric losses in the polymers is considered to be the internal motions or the local movements of the molecular chains of the polymer. At high temperature, especially at the glass transition temperature of the polymer such segmental

motions are prominent. How ever, at low temperature these motions become less significant.

4.3 (a) Frequency Dependence of Capacitance:

The capacitance and hence the dielectric constant of (fig. 4.1) iodine doped PS remains constant with the change in frequency. This is so because the polarization settles itself during a very short period of time as compared with the time of voltage sign change. Dielectric constantof non polar polymers remains invariable with frequency. In case of polar polymers, the dielectric begins to drop at a certain critical frequency and at very high frequencies it approaches the values typical of non polar polymers. In amorphous polymers structural polarization (i.e. related to the loose structure of matter) is also possible. For this type of polarization, the capacitance falls with the increase in frequency (354).

4.3 (b) Temperature Dependence of Capacitance:-

The increase in capacitance above the room temperature (Fig. 4.2 & 4.3) may be partly due to the expansion of the lattice and partly due to an ionic mechanism of paraization. The molecules can not orient themselves in polar dielectric (355)

FIG 4.5 Loss tangent Vs Iodine Concentration at 30°C and at a frequency of 2KHz.

30°C, 2kHz

Loss Tangent

CONCENTRATION
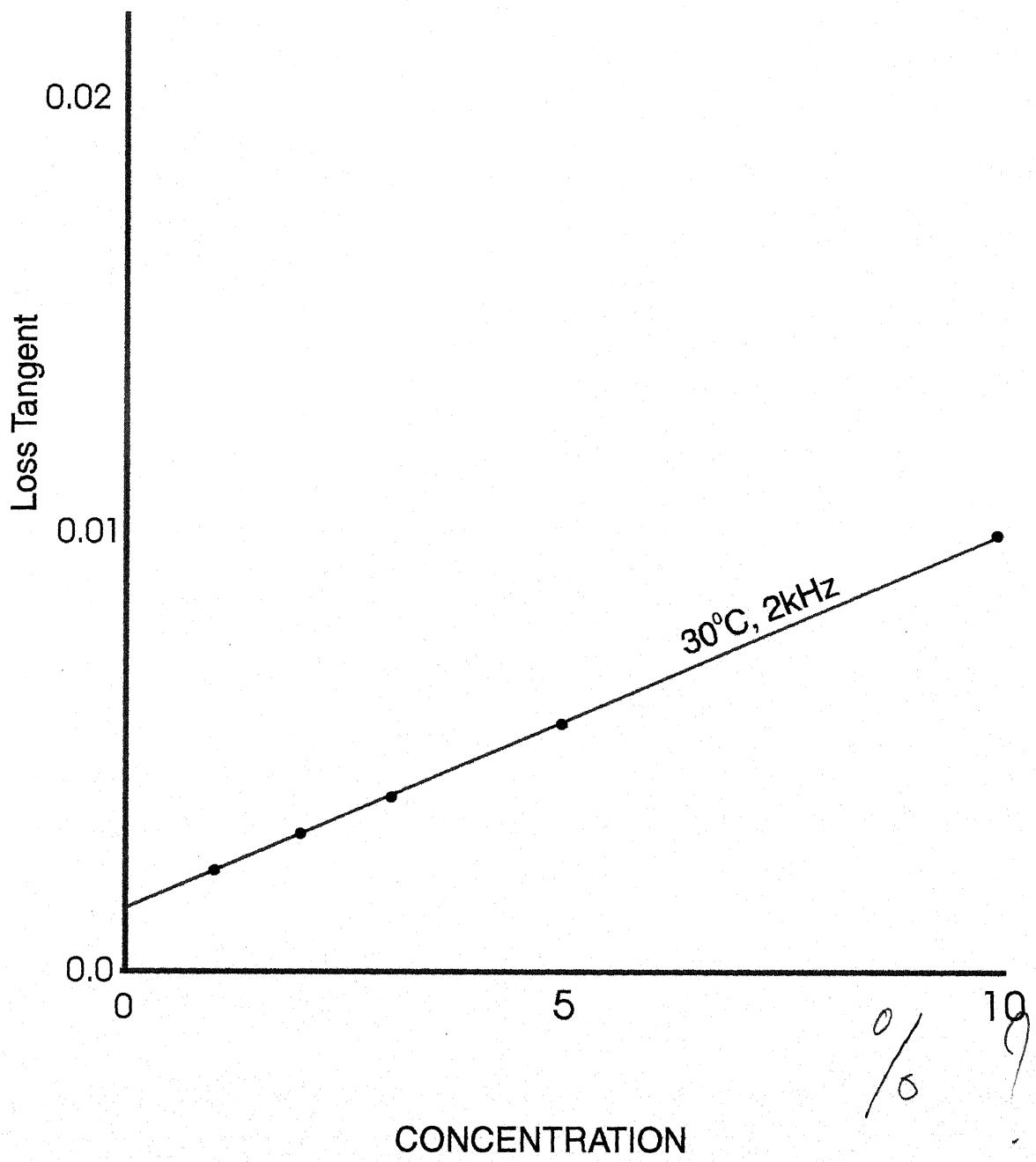
in the low tempreture region. When the temperature rises, the orientation of dipoles is facilitated and this increases dielectric constant. Addition of iodine may form charge transfer (CT) complexes with the polymer and so the increase in capacitance with temperature is enhanced.

4.3 (c) Variation in loss Tangent :-

Temperature transition corresponding to Alpha relaxation process has been observed near the glass transition temperature of PS (Fig. 4.4 & 4.5). The Alpha-relaxation process in polymer is observed at temperatures above the glass transition of the polymer. Though at glass transitioin temperature the segmental motion is expected but at the temperatures above the glass transition temperature some thing larger than segments and possibly the entire molecular chain motion is expected. Polymers are considered to be the mixtures of amorphous and crystalline regions. Above the glass transition temperature they seem to loose the intermolecular cohesive bondings and the association and dissociation processes involved are governed by thermodynamical equilibrium. Therefore, Alpha-relaxation process may be attributed to the motion of the more mobile molecular chains in which the intermolecular forces between the crystalline

FIG 4.6 Log Fmax Vs $10^3/T$ for PS and I_1
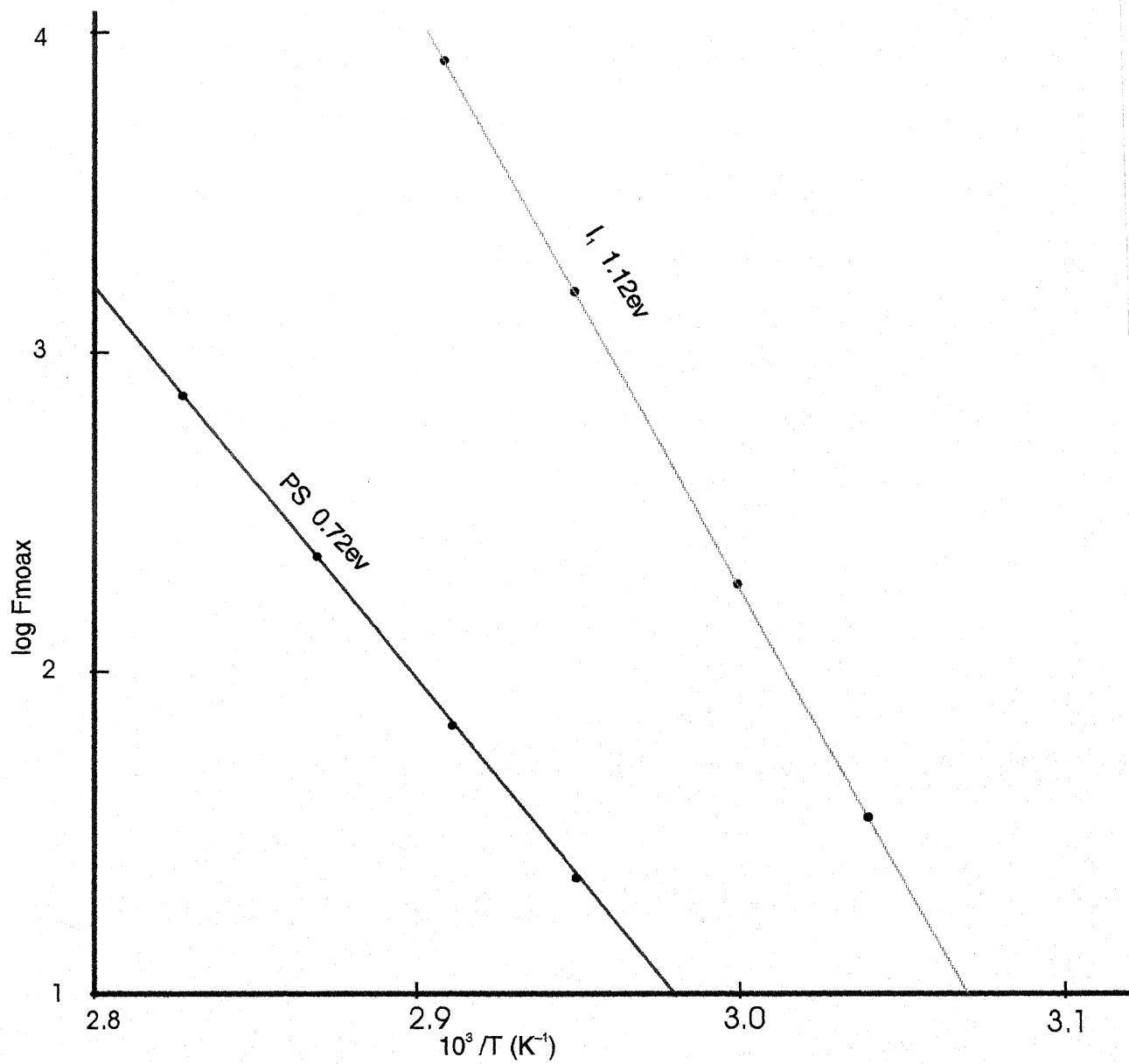
regions are weakened due to thermally activated process. This weakening of forces causes the motion of the entire molecular chain and hence the occurrence of Alpha-relaxation.

Incorporation of iodine in PS softens the viscosity of the system and causes the Alpha-relaxation to shift to the region of lower temperature. The view is further supported by the observation that the increase in iodine concentration has an effect of displacing the loss maxima to a lower temperature.

Logarithm of frequency at which loss maxima occurs, has been plotted against inverse absolute temperature in (fig 4.6) for pure and iodine doped PS films. The activation energy is calculated to be 0.72 eV for PS and 1.12 eV for I_1. Incorporation of iodine has an effect of increasing the activation energy. Besides molecular chain movements, the losses also occur due to electrical conduction which increase with the decrease of frequency. This is also what has been observed presently. Mixing of iodine in PS increases the conductivity of the film and so the doped films exhibit more pronounced increase in losses with the decrease of frequency.

4.4 Conclusions :

The present investigation on dielectric behaviour of pure and iodine doped PS films helps to conclude:

(1) Dipole polarization involving ionic motion is prominent in PS. Doping of the matrix with iodine enhances the process of polarization.

(2) The Alpha-relaxation in the polymer is due to the motion of polymer chains. Addition of iodine reduces the viscosity of the system shifting Alpha-relaxation peak to lower temperature.

(3) Doping causes conduction losses.

(4) Above the glass transition temperature of the polymer, main chains are mobilized and the mobilization is facilitated due to incorporation of iodine.

* * * * * *
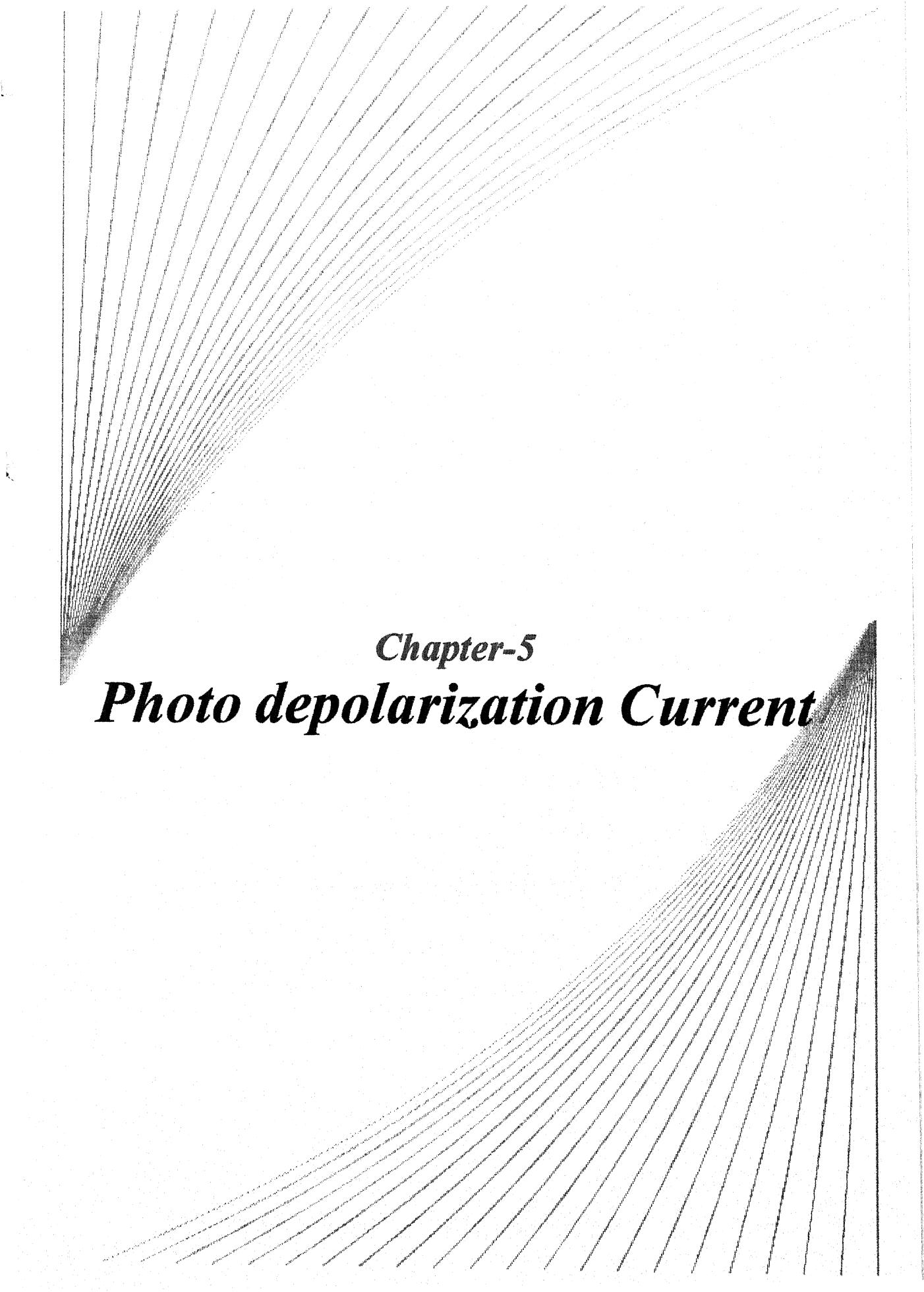
Chapter-5
Photo depolarization Current

PHOTO DEPOLARIZATION CURRENT

5.1 Introduction

Many polymers (356-371) show polarization effects when an electric field is applied in the presence of illumination. It is a problem of interest from stand point of the technology involved in using these materials in radiation environment and for the pieces of information, it gives on conduction process in insulating materials. The processes taking place during photo polarization and depolarization are the basis of persistent electrical photo graphy (356). Persistent internal polarization is a striking static phenomenon and supplies several important pieces of information which can not be easily obtained otherwise.

The studies have been made of the spectral characteristics and photo electric sensitivity of many organic polymers (372-395). In spite of the considerable number of papers devoted to photo electric sensitivity, so far, there has been no sufficiently well founded theory of the mechanism of photo excitation of current carriers and their transfer in polymeric structures. Never the less, the characteristics of photo conduction of several polymers give grounds for considering these materials

as promising substances for practical use. There are no experimental results available for polymeric semiconductors that could fully explain the processes of photo conduction. Such results have been obtained for low molecular weight semi conductors (396-399).

There have been a number of recent studies of photo-conduction induced in polymers with ultraviolet light. The most extensive investigation has been carried out on low density polyethylene for which it has been established that hole injection occurs from the anode. This observeation by Vermeuran. Wintle and Nicodema (400) has been confirmed by Commins and Wintle (401) and by Mizutani (402) who showed that hole injection regime is dominant only when the applied field is below 300 KV Cm^{-1}. The photo current varies linearly with illumination intensity (401) and with voltage (402). It exhibits no dependence upon the thickness of the specimen at constant voltage, indicating that the current is controlled by contacts (401), thus confirming an earlier suggestion by Wintle (403) and Tibensky (404) that photo injected charges traverse the full thickness of the specimen and are not permanently trapped because the illumination fulfils the subsidiary role of injecting any charges which may be trapped in

the bulk. These authors also showed that the dark absorption currents and the photo-currents were independent of one another and supported these observations with rough numerical estimates of the magnitude of the charge of each type in a typical experiment.

Hersping et al (405) have reported that polyvinyl chloride films exhibit a sensitive photo-conduction under the illumination of UV light. At the same time, however, Kryszewski et al (406) have observed the decrease of conductivity of polyvinyl chloride films under UV illumination, namely a negative photo-conduction. Mizutani et al (407) investigated photo-conduction of polyvinyl chloride in more detail and concluded that photo-conduction in the polymer is induced not only by UV light but also by visible and near infrared light unlike polyethelene in which photo-conduction is induced mainly by UV light.

Takai et al (408) have developed an experimantal technique to confirm the photo-injection from metal electrode and to determine the sign of the injected carriers and have applied it to polyethelene terephthalate in the wavelength region 400 nm to 320nm. The dominant carriers injected are electrons for

aluminium and copper and electrons and holes for silver at round 370 and 340 m respectively, but for the other they can not be determined due to the small photo injection currents.

These photo-injection process are mainly controlled by the work functions of metals and insulators, but can not be explained by the work function only and the surface states are tentatively proposed. Photo emission of electrons from metallic electrodes into poly N-vinylcarbozole and the threshold values of internal photo-emission change according to the work function of the metal have been investigated.

Recently there have been a few reports on photo polarization of doped polymer films (191, 192). Srivastava et al (191) study electrode effect on photo-polarization of copper phthalocyanine doped polystyrene films and investigate build-up of polarization (192) with field and time. These results on photo-polarization of doped polymer shows that life time of photo generated carriers can be greatly modified by doping the polymers with suitable impurities.

This chapter reports photo depolarization currents in iodine doped PS films and investigate the build-up of polarization

Fig. 5.1 Photo depolarization current Vs time, poling time noted on the curve poling voltage being 54V, for I_{10} Insert - Charge released Vs polarizing time.
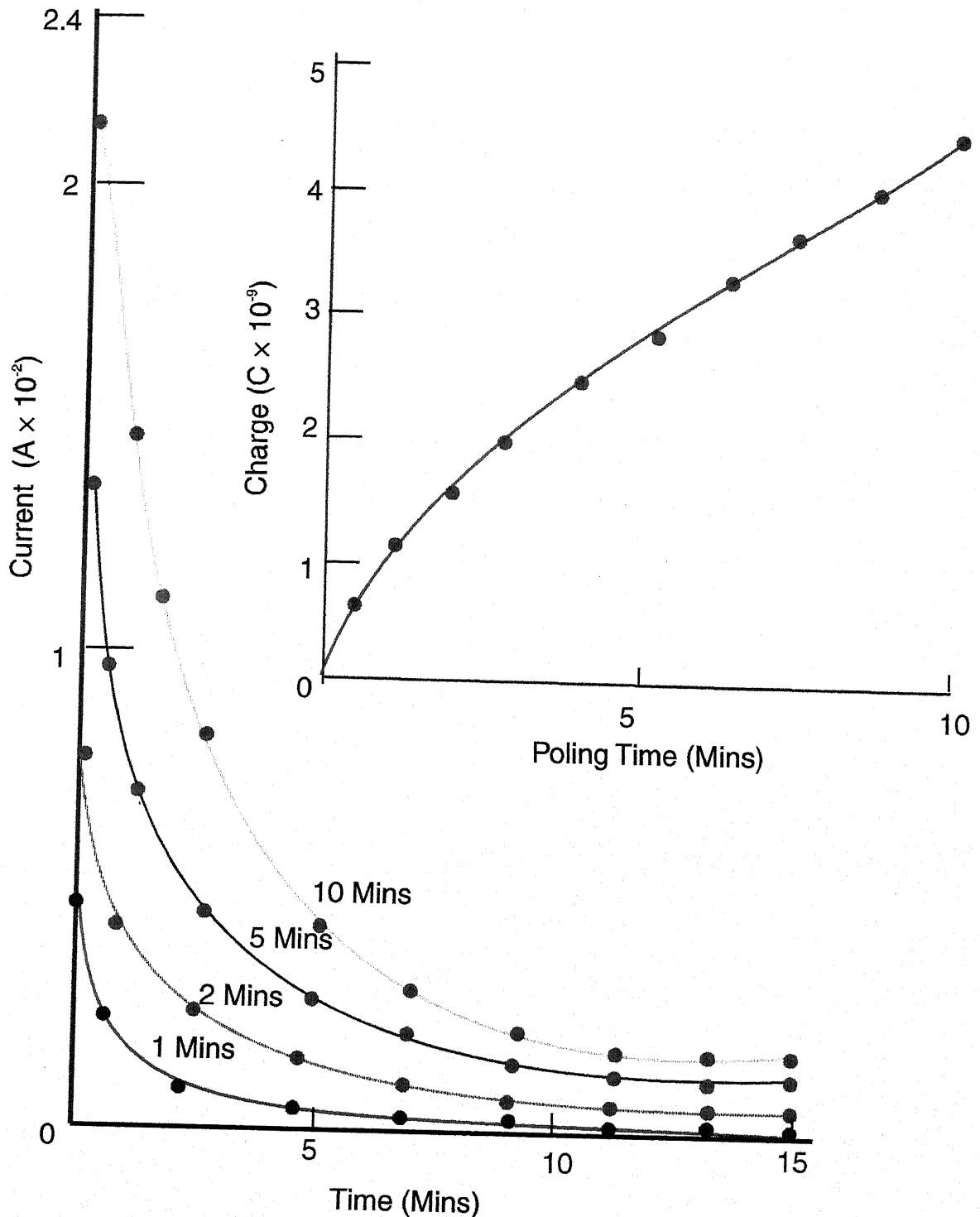
Fig. 5.2 Photo depolarization current Vs time, poling Voltage noted on the curve poling time being 15 Mins for I_{10}
Insert :- Charge released Vs Polarizing Voltage
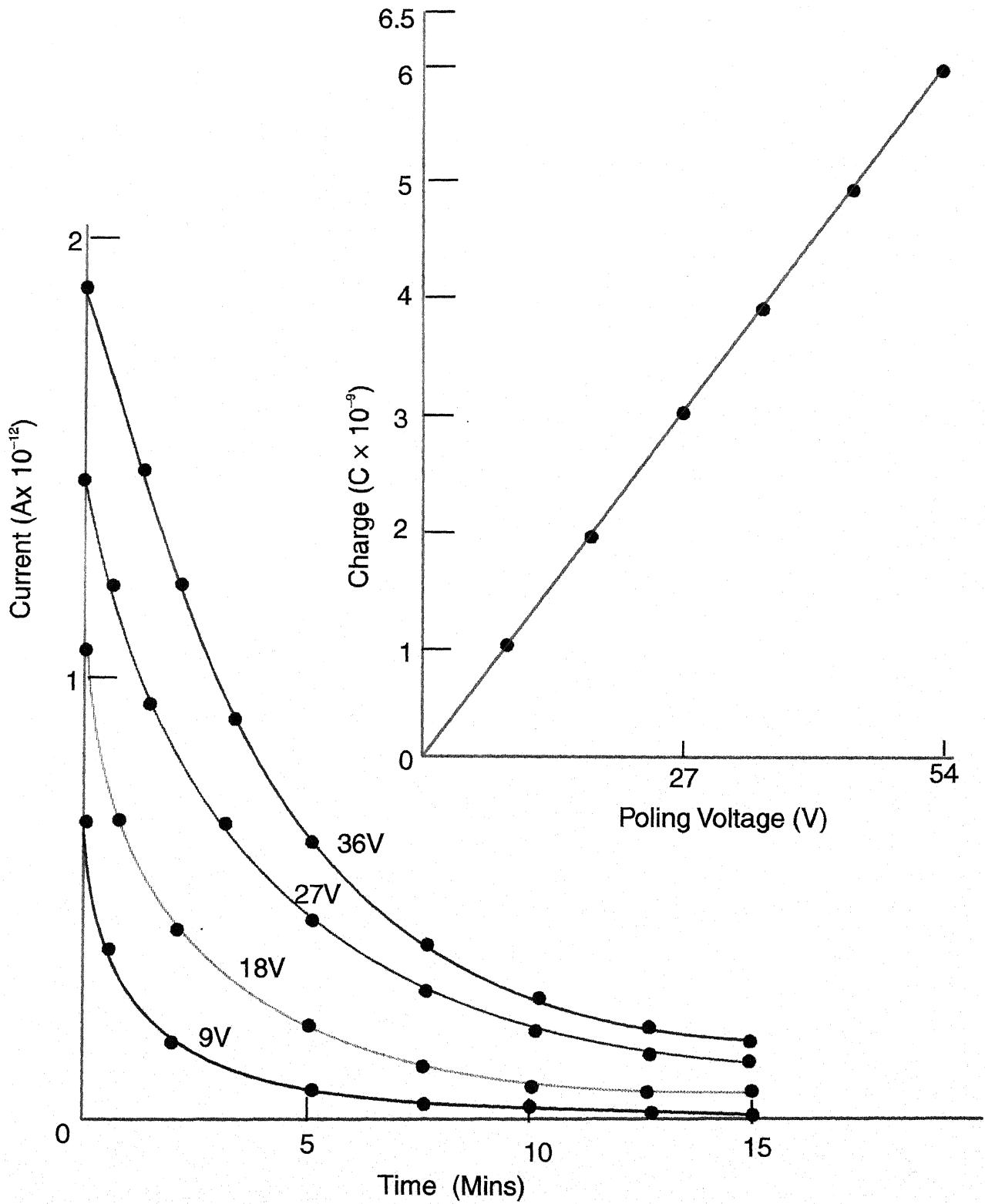
with field and time.The electrode effect on photo depolarization current is also reported.

5.2 Results :-

To investigate photo depolarization currents in iodine doped PS films, the samples I_1- I_{10} were used. Time of photo polarization was varied from 1 to 10 minutes and the voltage applied was changed from 9 to 54V. The photo electrets formed, were kept short-circuited in dark for 30 seconds to minimise stray charges and then were depolarized by reirradiating them with the same UV light which was used during polarization. Photo depolarization currents Vs time as a function of poling time is shown in Fig. 5.1. Sample I_{10} was used and The voltage applied was 54V. As poling time is increased, initial and final value of current is increased. Charge released during the depolarization was calculated by integrating current Vs time curve. Charge Vs poling time has been plotted in the insert of fig. 5.1. The plot is not a straight line. Charge released increases first rapidly and then slowly with the increase in polarizing time. Photo depolarization current Vs time for various polarizing voltages have been plotted in fig 5.2. Film I_{10} was polarized for 15

Fig. 5.3 Initial photo depolarization current Vs square root voltage

Intial Current (A x 10^{-12})

$\sqrt{V}$
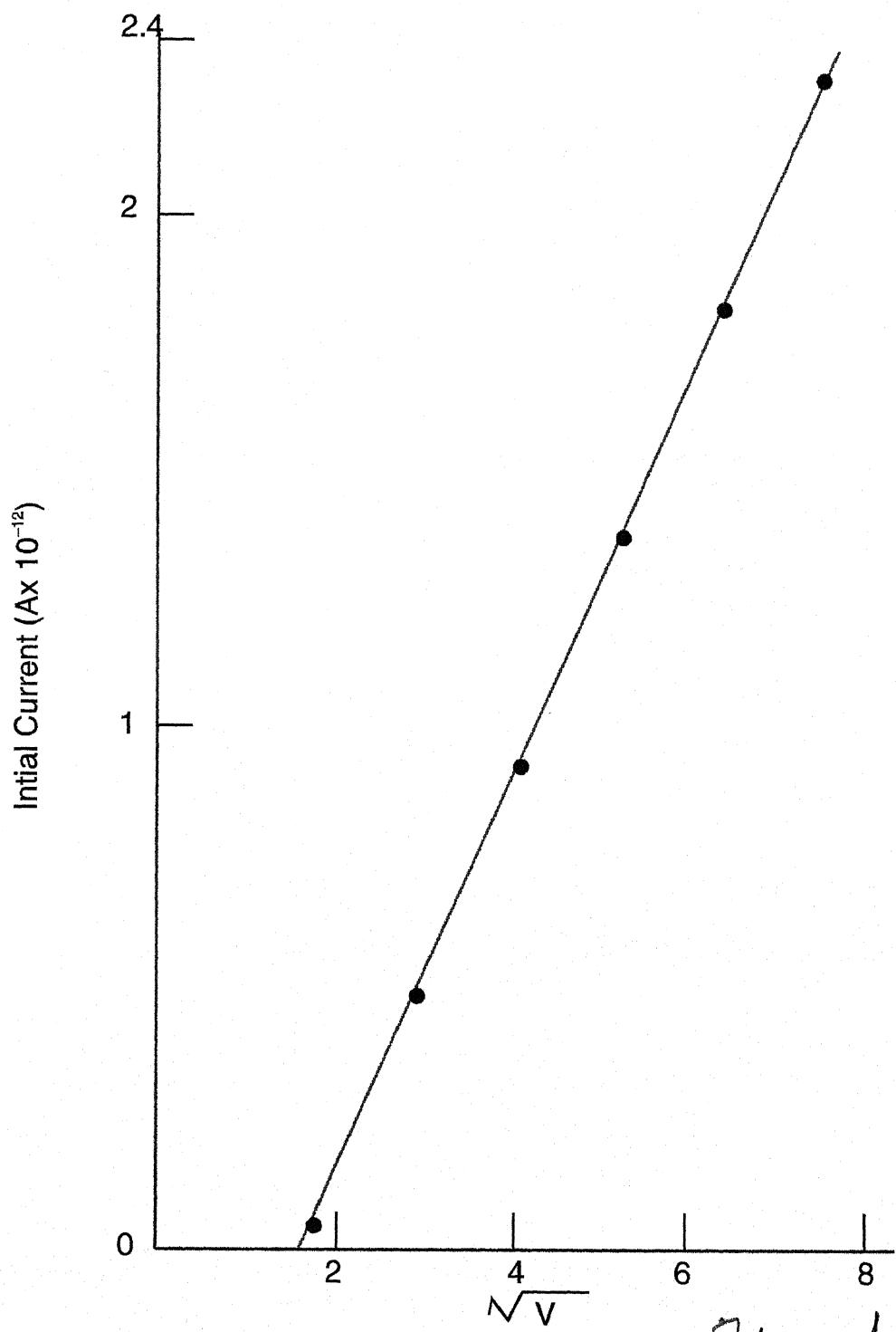
units ?

Fig. 5.4 Effect of iodine concentration on photo depolorization current Vs Time, poling time being 15Mins, poling voltage being 54 V Insert :- Charge Vs Time
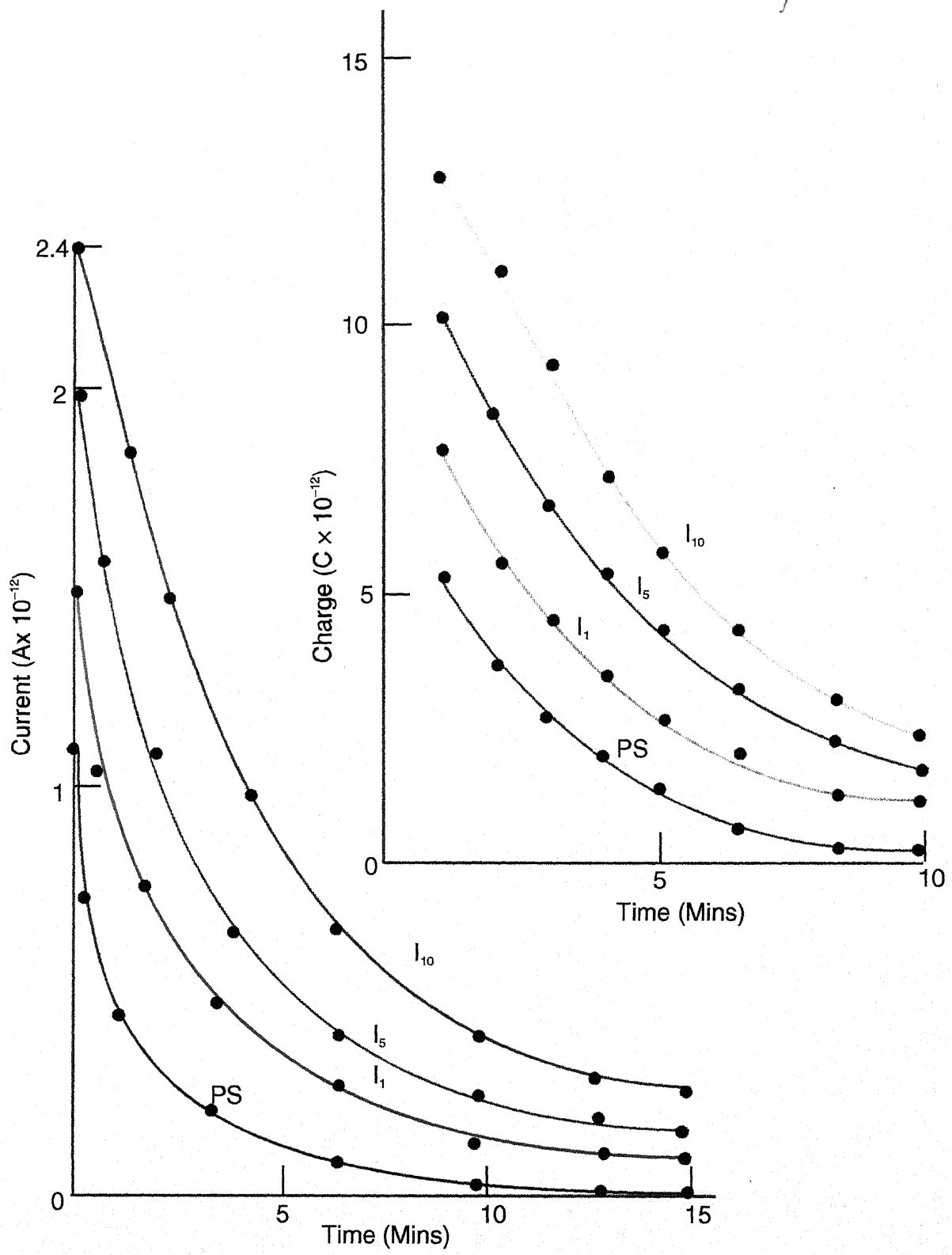
minutes. As the poling voltage is increased, initial and final values of current are increased. Charge released Vs polarizing voltage has been plotted in the insert of fig 5.2. The charge released increases linearly with poling voltage upto 54V. Initial photo depolarization current Vs square root voltage is shown in fig 5.3. The plot is a straight line. Effect of iodine concentration on photo depolarization current decay mode has been shown in fig. 5.4. For this purpose, films I_1, I_5 and I_{10} were poled by 54V for 15 minutes. For the sake of comparison, photo depolarization current decay mode for pure PS film is also included in the fig 5.4. Charge released Vs time of decay for these films has been plotted in the insert of fig 5.4. Initial and final values of current and charges are increased due to increase in iodine concentration.

To study the effect of electrode material on photo depolarization current, films I_{10} grown on Cu, Ni and Zn substrates were poled for 15 minutes by 54V. The current decay modes have been shown in fig 5.5 Current changes drastically due to change in electrode forming material. Initial and final depolarization currents Vs work function of metal have been plotted in the insert of fig 5.5. The plots maybe considered to be nearly linear. The currents are seen to decrease with the increase

in metal work function.

5.3 Discussion :-

When the absorption spectra and photo conductivity spectra for the majority of polymers are compared, a direct correspondence between them can be found. At the same time, by analogy with low molecular weight organic semiconductors, it may be assumed that light causes singlet-singlet transitions (409). The absorption of a photon in a polymer leads to the formation of an excition which can migrate freely within the limits of a region of conjugated bonds. Cherkasov et al (410) in an interpretation of the absorption and diffue reflection spectra of polystyrene have indicated the possibility of formation of free carriers by dissociation of excitons generated by optical excitation. Preliminary irradiation of the polymers with UV light greatly increases their photo conductivity and it may be argued that UV light can ionize conjugated molecules, liberating photo electrons, which are retained in the structure of the polymer and creating positively charged local centers which can serve as electron traps. On long wave irradiation, excitons are produced which are destroyed on defects (including defets created by UV

radiation) withthe formation of a trapped electron and a mobile hole. When a photo conducting material is illuminated with radiation, electrons and holes are produced. If a d.c. voltage is simultaneously applied across the sample, these holes and electrons move to negative and positive terminals respectivily. At any given temperature, a number of defects are usually present in a material. So there will be a number of trap levels present in the energy gap due to the interactions of these impurities with the ions of the sample. These defects can capture a hole or an electron. Thus the carriers generated by the photons can be trapped in certain levels in the material. These trapped hole and electrons give positive and negative charges on either side of the sample.

The total current produced while reilluminating the sample can be due to two effects (411)

(a)   Current due to the motion of carriers generated by photons and

(b)   Current due to dark polarization

The former (a) is given by

$$J = J_p + J_n \qquad \qquad ..... 5.1$$

ω Where $J_p = p.e.\mu_p E$

~~and~~ $J_n = n.~e.~\mu_n E$

and ~~Where~~ n and p are number of electrons and holes created by photon irradiation, μ_n and μ_p are mobility of electrons in conduction band and holes in valence band. E is the electric field.

So this current depends mainly on the number of carriers ejected out of their traps due to reillumination of the sample. The (later) *latter* (b) includes the currents produced by :

1. The motion of ions which have been displaced during polarization.

2. The decay of stripping charges produced by the close contact of the metallic electrode and the dielectric.

3. The decay of the sprayed ions from the electorde on the surface during polarization especially at high fields, and

4. The thermal current which depends on the temperature of the sample.

During the depolarization two main processes are taking place:

1. The ionic charges and stripping charges produced due to dark polarization decay by recombination and lattice relaxation

processes. This decay is very slow.

2.   A number of electrons and holes trapped near the conduction and valence bands first get sufficient energy to come out to the conduction and valence bands repsectivily to contribute to the flow of current. As time goes on the current decays gradually which means that the numbers of free carreirs decreases. At this time the current contribution comes mainly from carriers which are trapped well inside the energy gap and requires sufficient energy to get themselves in to the conduction and valence bands.

It has been possible to observe the spectral sensitization of the photo effect in polymers, in particular polymers with triple bonds and polyacetylides. Two explanations exist for the sensitization of polymers due to doping (412). One connects this effect with the transfer of excitation energy from the absorbed molecules of the dopant to the carriers trapped in the local levels. and their excitation in to the conducting state. According to the other model, the process of sensitization consists in the transfer of an electron from the dopant to the semi-conductors. Since some of the dopants do not posses photo electric sensitivity, the first mechanism is preferable. Because

sensitized photo-conduction is carried out by holes, the transfer of excitation energy to the polymer apparently leads the ejection of an electron from a completely filled band into local levels with the liberation of holes taking part in photo conduction or (which is the same thing) to the excitation of holes into the valence band from the trapping levels.

The observed change in the intrinsic photo electric sensitivity of a polymer in the presence of a dopant is not yet completely clear and is possibly connected with the nature of the traps created by the absorbed molecules of the dopant. The increase in the photo conduction of the polymer on the addition of traces of iodine may be regarded as a peculiar sensitization phenomenon. In this case the influence of the iodine may be exerted by the second mechanism.

5.3 (a) Current Decay mode:

Depolarization current decay modes of iodine doped photoelectrets (fig. 5.1 and 5.2) consists of two parts. Initially the current decays rapidly and then slowly. The rapid decay of current is associated with the holes while in the slow decay region, current is mainly contributed by the electrons (413). The

Fig. 5.5 Effect of electrode material on photo depolorization current Vs Time, poling time being 15Mins, poling voltage being 54 V for I_{10}

Insert : Initial & final currents Vs metal work function
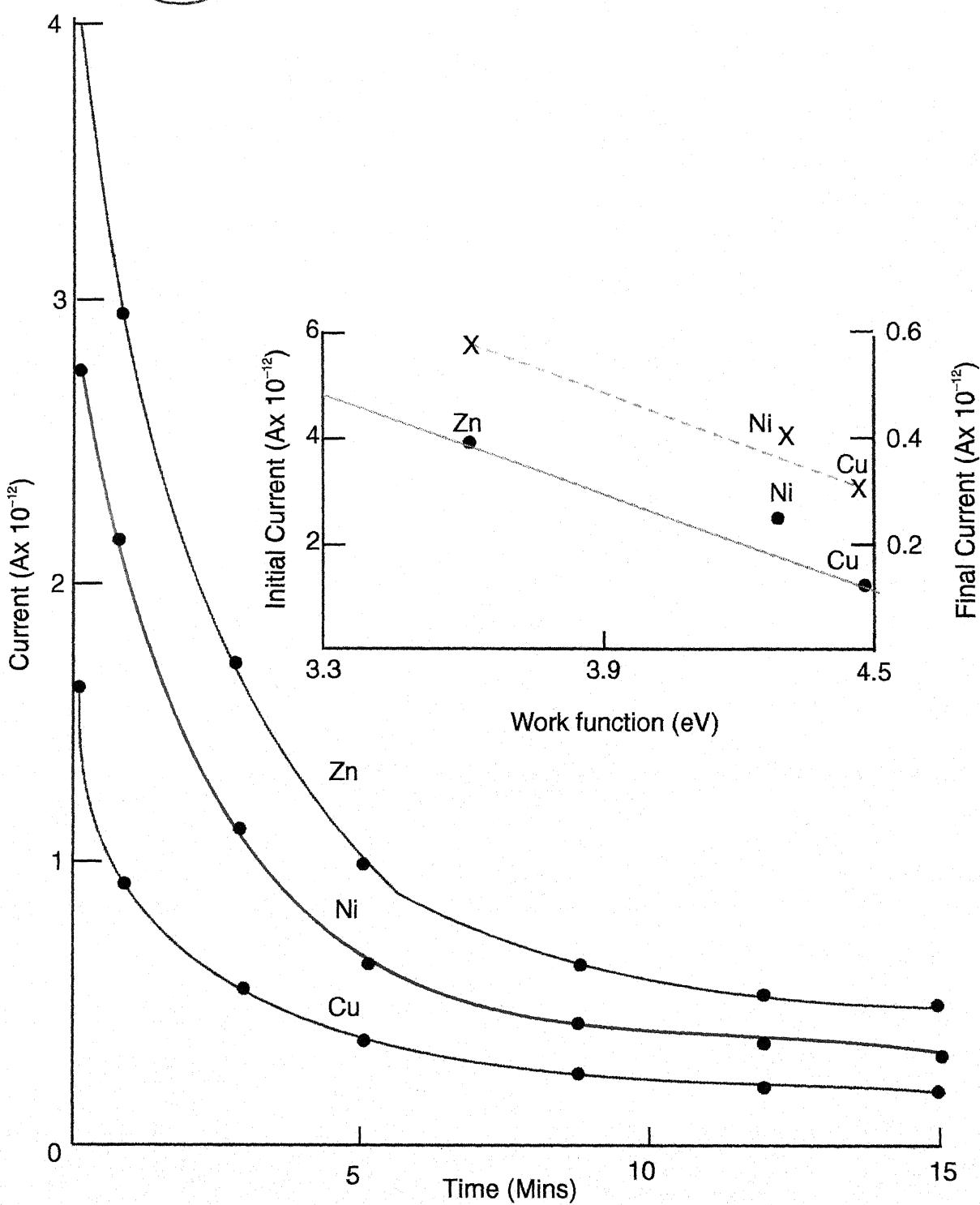
Fig. 5.6 Replot of fig 5.4 Activation energy noted on the plot
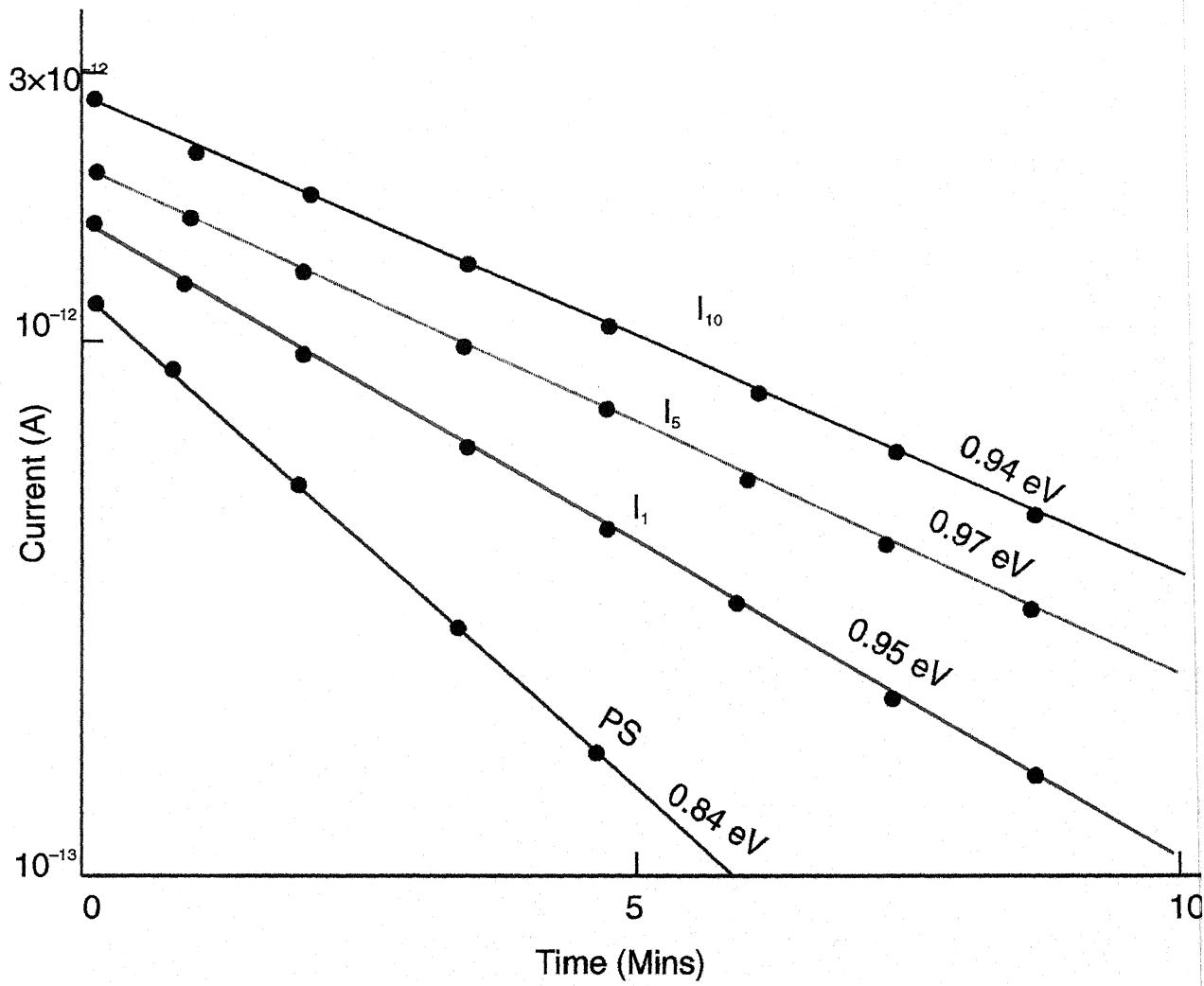
holes are trapped weakly close to the boundary levels and the electrons display a spread in the bulk. The exponential decay of current i (t) can be dscribed by (414)

$$i = i_0 \exp(-t/\tau) \qquad \qquad ....5.2$$

where i_0 is the initial current and τ is the relaxation time which is represented by;

$$1/\tau = \nu_0 \exp(-E/kT) \qquad \qquad ...5.3$$

where ν_o is the frequency of escape from the trap. E the activation energy for the traps, k Boltzmann constant and T the absolute temperature. The slope of the plot of fig. 5.6 yeilds the value of τ and taking $\nu_0 = 10^{12}$ trap depth is calculated. These values are noted in fig 5.6 for PS activation energy is calculated to be 0.84eV. Due to doping, it is increased. There is no regular variation in activation energy with the dopant concentration.

No appreciable energy differences are found between shallow and deep traps in the two types of films. However, it may be said that doping ofthe matrix with iodine has an effect of increasing the trap depth. This fact can not be explained if it is assumed that mobile charges are produced as a primary process of light absorption but is easily understandable in terms of

Fig. 5.7 Replot of fig 5.4 in the form charge Vs log time. Insert shows total charge released Vs Iodine consentration.
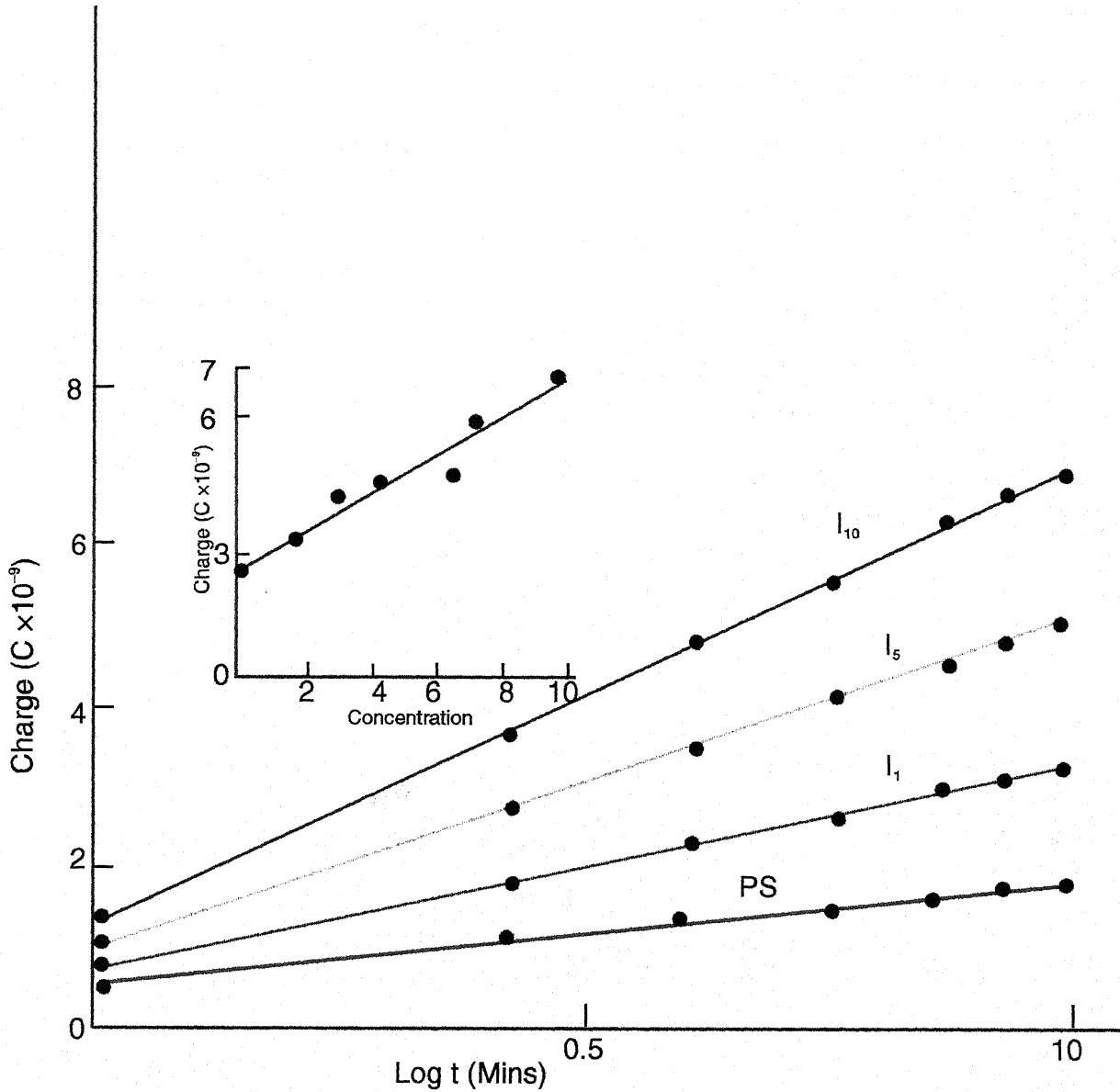
creation of free charges via exciton formation (415) where doping reduces the relaxation time.

The decay mode of depolariztion current seems to be hyperbolic rather than exponential. The validity of the hyperbolic decay law can be checked by integrating current versus time to obtain the flow of charge (Q) upto time (t) which is found to be

$$Q = 1/B \log (1 - B \, i_0 \, t) \qquad \qquad ...5.4$$

where B is a constant of proportionality when $B \, i_0 t \gg 1$

$$Q = 1/B \log B \, i_0 \, t \qquad \qquad ...5.5$$

Therefore Q versus log t should be a straight line. Fig 5.7 shows these plots of pure PS and of I_1, I_5 and I_{10}. The inset of fig 5.7 exhibits total charge released as function of iodine concentration. Straight line plots of fig. 5.7 suggest hyperbolic decay law of current.Consequently, the dissipation of the states of polarization is bimolecular in nature (416, 417).

5.3 (b) Polarization versus time :-

The field effect on polarization is understandable when the dependence of polarization on time is taken into account, charge released as a function of electret forming time has been shown in fig. 5.1 for I_{10}. The build-up of polarization (P) with time is

seen to have the form (18).

$$P = P_{max} [1-exp (t/\tau)]$$ 5.6

The slowing down of the rate of increase of polarization results from the fact that as the polarization builds-up, the effective field on mobile charge decreases.

5.3 (c) Build-up of polarization with field:

Released charge versus polarizing voltage (fig. 5.2) for PS is characterized by a straight line passing through the origin. This shows that there is a voltage dependent source of electrons. This may be in the bulk or at the negative electrode. Initial depolarization current Vs square root voltage plot (Fig 5.3) supports the trap filling hypothesis (418). At high fields the increase in polarization is slowed down because of the saturation of the number of traps available for polarization. When all the traps are filled, any holes and electrons will recombine rapidly. Iodine forms charge tranefer complexes with PS and creates new trapping sites (414) in the matrix exhibiting enhanced polarizability.

5.3 (d) Electrode Effect :-

Considerable electrode effect on photo-

Fig. 5.8 Replot of fig 5.5 in the form charge Vs log time. Insert shows total charge released Vs work function
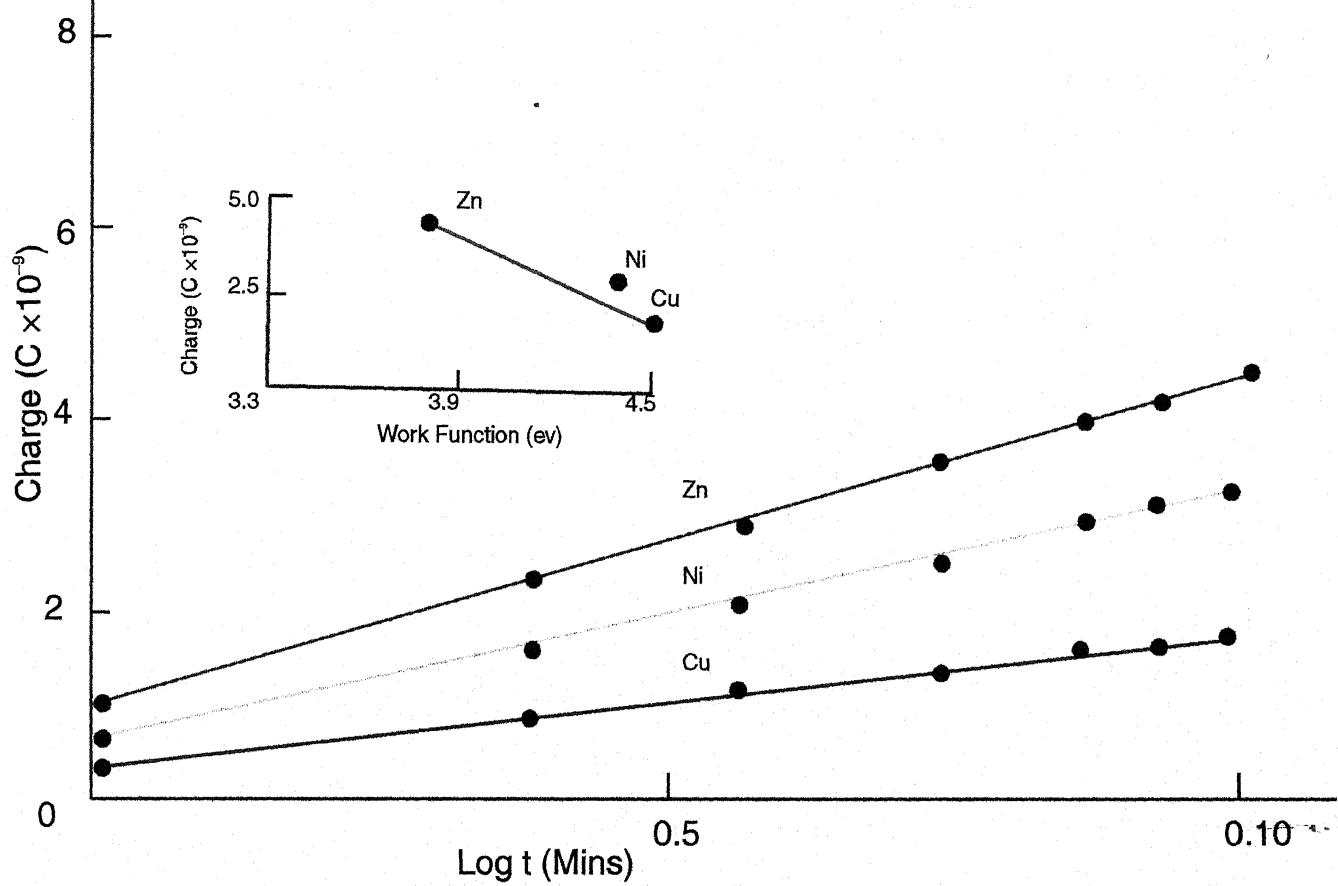
depolarization current in iodine doeped PS films has been observed. The asymmetry between the current and the charge released at the electrodes indicates the majority of holes (122). Incorporation of iodine in the polylmer creates a high density of trapping centers (419) and so the doped films store more charge. The presence of impurties in the polymer reduces the life time of the excitons increasing the probability of formation of mobile charges via excitions. In the insert of fig 5.5 the initial maximum and final values of depolarization currents have been plotted against metal work function. The plots are straight lines showing the the amount of charge carriers, supplied by the metal and injected into the sample increases with decreasing metal work function (420). Fig 5.8 is the replot of 5.5 in the form charge Vs log time. The plots are straight lines and indicate hyperbolic decay law. The insert of fig 5.8 shows total charge released Vs metal work function. This is a straight line, again supporting that charge injection from electrodes decreases with the increase in work function. The present results of electrode effect on photo-depolorization current can be quantatively understood in terms of dielectric loss model (421) based on the tunnelling of electrons from the metal into traps located within the polymer near the

interface.

5.4. Conclusions :

Photo-depolarization current studies of iodine doped PS films enable one to draw the following conclusions.

1. Decay of depolarization current occurs in two parts. The rapid decay is due to detrapping of holes while the slow one is due to untrapping of electrons.

2. Iodine forms charge transfer complexes with PS and creates new trapping sites in the matrix enhancing the depolarization current and released charge.

3. Linearity of released charge versus field indicates charge injection mechanism.

4. Electrode effect on depolarization current indicates that the charge injection from electrode increases with decreasing metal work funtion.

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Chapter-6
Thermally stimulated discharge current

THERMALLY STIMULATED CURRENT

6.1 Introduction

Many kinds of polymer films (422-482) polarized in a high d.c. field at an elevated temperature and cooled in that field, have semi permanent charges which exist for many years at room temperature. Depolarization currents at room temperature are frequently too small to be easily measured. To increase them one must speed up the depolarization process by heating the electret upto or above the polarization temperature. The ensuing current has been called thermally stimulated current (TSC), since it is produced by heating without an external voltage (483). TSC is now generally considered as particularly well suited to the study of dielectric relaxations (484-512). This is mainly because this technique is characterized by a very low equivalent frequency as compared to the dielectric loss method and consequently leads to a better resolution of the different relaxation processes (513).

As a matter of fact, the α, β relaxations arising from the conformational motions of main chain segments and from the local motions of main chain or side groups respectively are more or less superimposed at the common measurement frequencies of

a few hertz and thus the values of the characteristic parameters determined from the loss curves are often hybrid values (514). Much uncertainly results from this and numerous discussions are found in the literature especially concerning the detailed mechanism of the motions involved (514, 515). the discrete or continuous nature of the possibly associated distribution of relaxation times (485) and the physical significance of such a distribution (501). With these last problems in view, the TSC technique appears also very useful, owing to its component peaks by techniques such as thermal cleaning or partial polarization (517).

A wide literature (515-584) is availaable on TSC in polymers. The technique has been widely used in the study of trapping parameters in luminescent and photo conducting materials. Lilly et al (585) investigated TSC in mylar and teflon. Stupp and Carr (586) suggested an ionic origin for high temperature discharge currents in poly acrylic nitrile. Guillet and Seytre (587) conducted a detaild study of the complex relaxation modes observed in poly-L-proline. Takeda and Naito (588) studied temperature change of dielectric constant of polystyrene using TSC measurement. TSC in corona charged polymers have been

investigated by Perlman (523) and those in electron beam irradiated, polymers have been investigated by Sessler (589). Ong and Turnhout (484) have concluded in favour of the existence of a continuous disrtibution of relaxation times. Recently similar conclusions have been inferred by Fischer and Rohl (590) and Hino (591) from studies on secondary peaks of polyethylene and polyethlene terephthalate respectively. Chaitan et at (518), however, have found in polyamides that the low temperature peaks could generally be decomposed in several discrete Debye processes.

It has been shown by theoretical argument and by experiments (592) that only is the case of a first order kinetics, polarization do the TSC peaks occur invariably at a fixed temperature. Otherwise, their position is shifting in a characteristic way with changing initial polarization. In the case fo a space charge release, for example, the peak temperature is increasing with polarization temperature and with polarizing time. Thus peak position data for varying polarization conditions allow one to decide in particular whether a peak is due to a first order depolarization process e.g. complex reorientation or to the release of a space charge.

TSC of polar materials (593) shows several bands or peaks. This indicates that the depolarization is realized by several different processes. Two such processes are well known, the relaxation of aligned dipoles and the relaxation of a space charge caused by mobile carriers accumulated at the electrodes. But there are still other processes which cause TSC peaks and have not yet been identified. It is one of the fundamental problems of any TSC investigation to relate the observed peaks to specific depolarization processes. TSC peak may be characterized by the maximum positions, the magnitude of the peak and the slope of intial rise of the peak. The magnitude of the peak is eventually a measure of the number of defects causing the polarization. The determination of activation is a delicate task if the peaks overlap too much, possibly no meaningful value can be obtained at all. Dependence of peak position on initial polarization provides information on the depolarization process.

TSC specta are unique to the material under study. They are finger prints of them and are sensitive to impurities, additives discharges, humidity i.e., to any chemical or morphological change. They provide a sensitive analytical tool that could be used to guide the production of materials with fixed

electrical properties. TSC is an electrical spectroscopy and has practical application to electrical quality control. Recently several workers (594, 595) have used TSC technique to investigate changes produced in polymers due to doping of them with suitable impurities. Gupta and Tyagi (594) doped polyvinyl fluoride with rhodamine, alizarine, dichloro-flurrecein and iodine and utilized TSC to find out the changes produced by doping. Srivastava et al have reported relaxation parameters by doping polystyrene with copper-phthalo-cyanine, ferrocene, anthracene, pyrene, iodine (66) and chloranil (595).

Mehendru et al (596) have reported TSC in PVAC films. They observed three TSC Peaks at 53, 116 and 195^0C and studied the effect of film thickness on TSC spectra of PVAC. The 53^0C peak was found to grow slightly with thickness. The magnitude of 116^0C peak was observed to increase with film thickness and 195^0C remained uninfluenced with the thickness. Total charge under all the three peaks grew linearly with the film thickness which led them to conclude uniform volume polaization in PVAC. Effect of iodine doping on TSC spectra of PVAC has been considered by Mehendru et al (597).

This chapter reports TSC in iodine doped PS films by varying, polarizing field, iodine concentration and electrode materials.

6.2 Theory:-

According to Creswell and Perlman (598), the instantaneous value of depolarization current i (T) when the sample is heated at a rate of $\beta = dT/dt$ (T being the temperature and t, the time) in terms of an activation energy H of the process involved, may be written as:-

$$i(T) = A \exp\left[-H/kT - B\int_{T_0}^{T} \exp(-H/kT)dT\right] \quad ...6.1$$

Where H is given by:

$$\tau = \tau_0 \exp(H/kT) \quad\quad 6.2$$

The temperature dependent expression in brackets is the same as obtained by Bucci et al (599), for the dipolar decay. The values of A and B for trapping near the surface are:

$$A = (N_0 \, e\delta^2)(\mu\tau)/2\varepsilon \, d\tau \quad ......6.3$$

$$B = 2/\beta\tau$$

and for dipolar decay, they are

$$A = Np^2 \, E_f / 3kT_f t_0 \quad\quad 6.4$$

99

$$B = 1/\beta\tau$$

Where N_0 = initial charge density in traps.

$\mu\tau$ = Charge mobility free life time product.

δ = Penetration depth of charge.

ε = Dielectric permittivity.

d = Sample thickness

e = Electronic charge

N = Dipole Concentration.

p = Dipole Moment.

E_f = Electret forming field.

T_f = Electret forming temperature.

k = Boltzmann's Constant.

τ_0 = Inverse of the trap escape freequency

and T_0 = The temperature at which the heating is started. Eqn. 6.1 shows a maximum at a temperature T_m given by

Dimensionally

$$\tau_0 = \frac{kT^2_m}{H \exp (H/kT_m)}. \qquad ...6.5$$

The current initially just above T_0 in equ. 6.1 can be shown to have the form $\log i (T)$ Constant - H/kT ... 6.6

The activation energy H for the discharge process responsible for a peak, can be obtained from a plot of $\log i(T)$

Vs 1/T. This is the initial rise method of Garlick and Gibson (600). It may also be calculated from Gross Weiner's formula (601).

$$H = \frac{1.3 \times 10^{-4} \, T_m T_h}{T_m - T_h} \qquad \ldots 6.7$$

T_h is the temperature corresponding to the half height of the peak on the lower temperature side of the curve. The attempt to escape frequency $v = 1/\tau_0$ can be calculated from eqn. 6.5. The capture cross-section (σ) could also be estimated from the relation (579).

$$\sigma = \frac{v}{2.9 \times 10^{24} \, T_m^2} \qquad \ldots (6.8)$$

Total charge release $\propto = \int i(t) \, dt \qquad \ldots (6.9)$

Using an approximation to the integral in eqn. 6.1. It is possible to write

$$i = A \exp[-H/kt - B\{\exp(-H/kt)\}(H/kT)^{-2}] \qquad \ldots 3.10$$

Using the Çowell and Woods (603) curve fitting technique with an initial low guess of H, then increasing it in small steps, it is possible to determine H and τ_0. The eqn. 6.1 can also be written in the form

$$N = [\int_t^\infty i(t) \, dt / i(t)] = \log(1/B) + H/kt \qquad \ldots 3.11$$

Fig. 6.1 Unpoled TSC Vs. iodine concentration
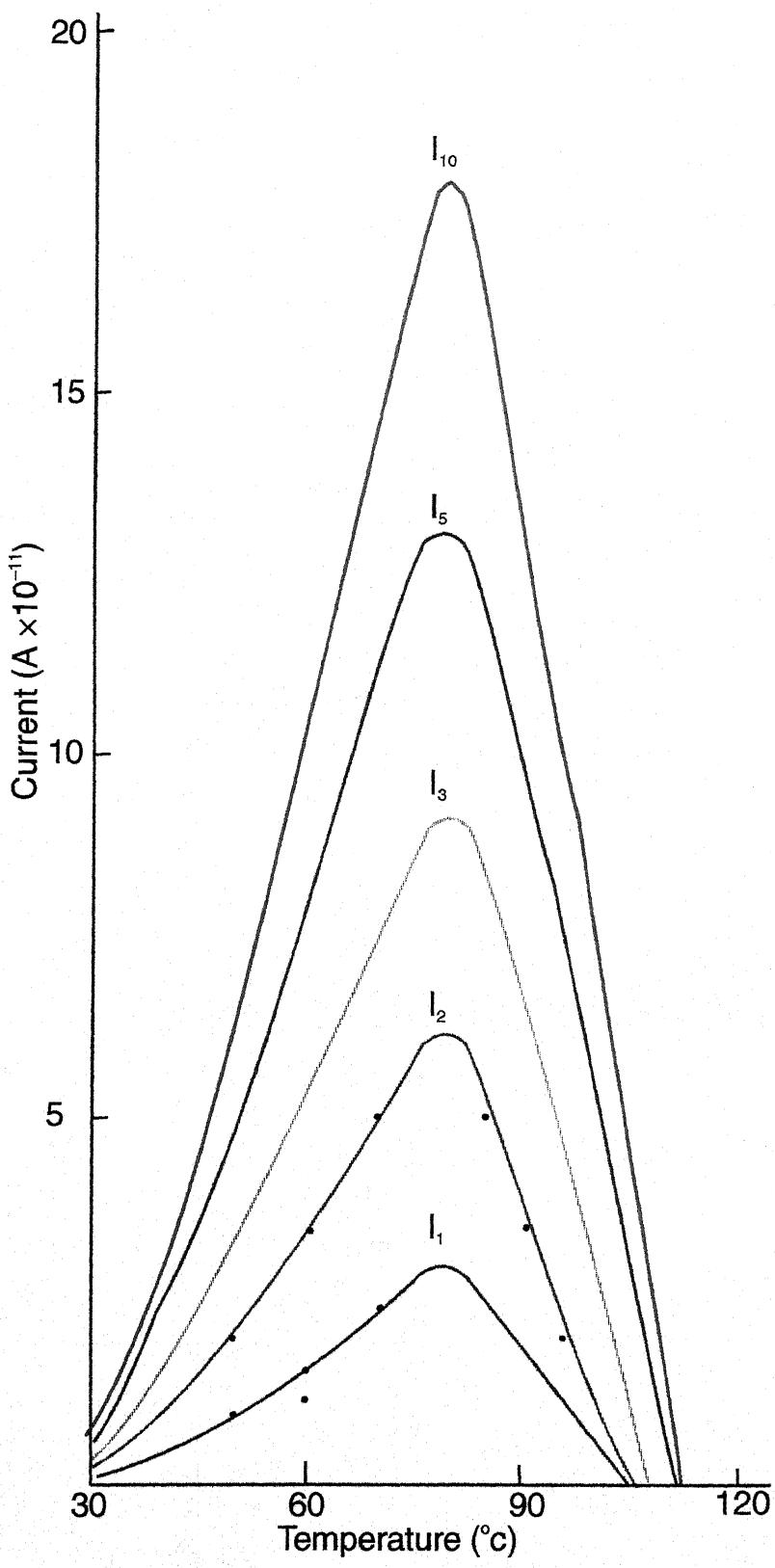
Fig. 6.2 Peak Current Vs. Iodine Concentration

Fig. 6.3 Inital rise plots of Fig 6.1
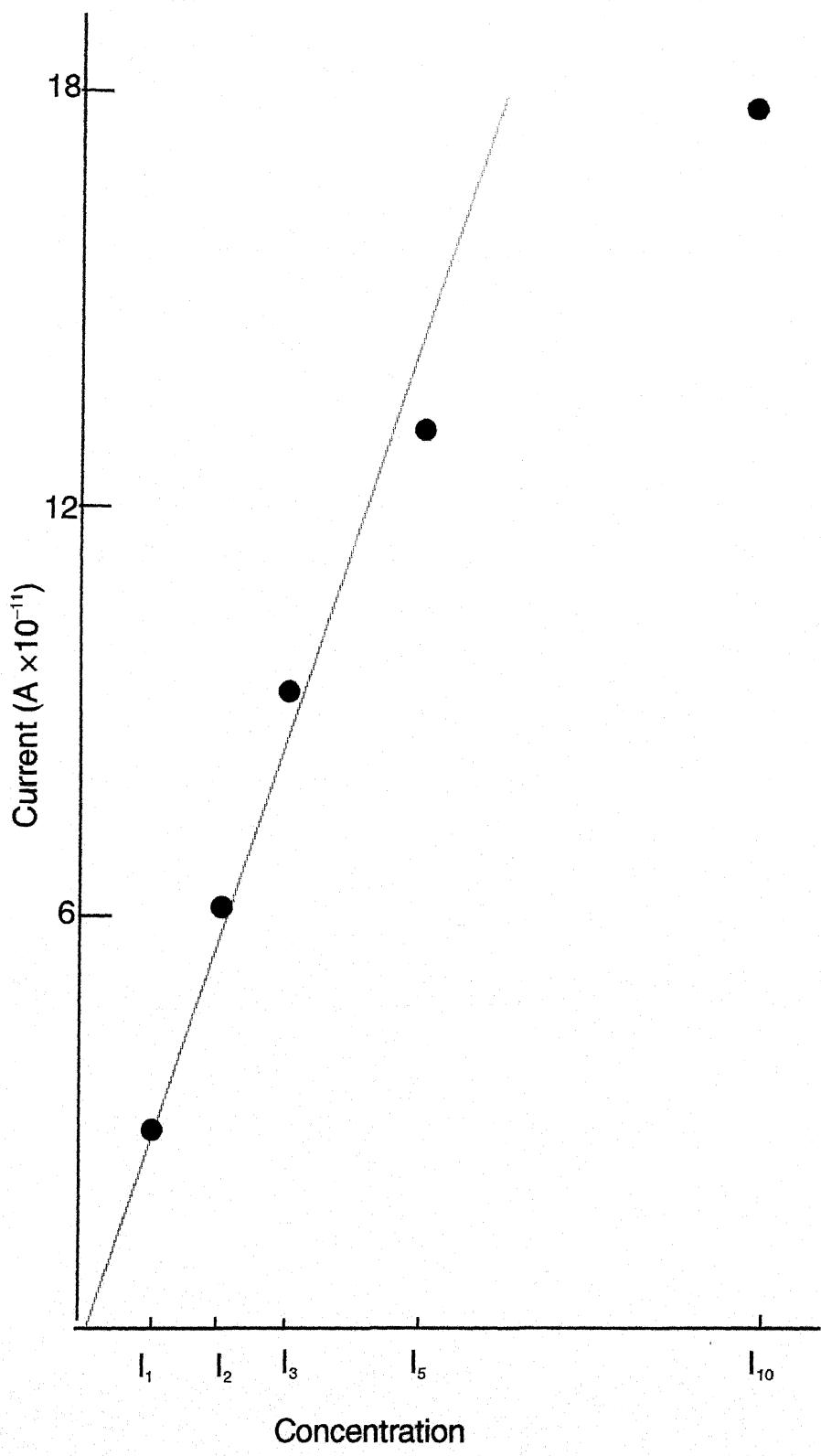
Plot of Current (A) versus $10^3/T$ (K^{-1}). Y-axis labeled Current (A) ranging from 10^{-11} to 2×10^{-10}. X-axis labeled $10^3/T$ (K^{-1}) ranging from 2.9 to 3.3. Curves labeled with activation energies 0.26 eV (I_{10}), 0.34 eV (I_5), 0.34 eV (I_3), 0.34 eV (I_2), and 0.48 eV (I_1).
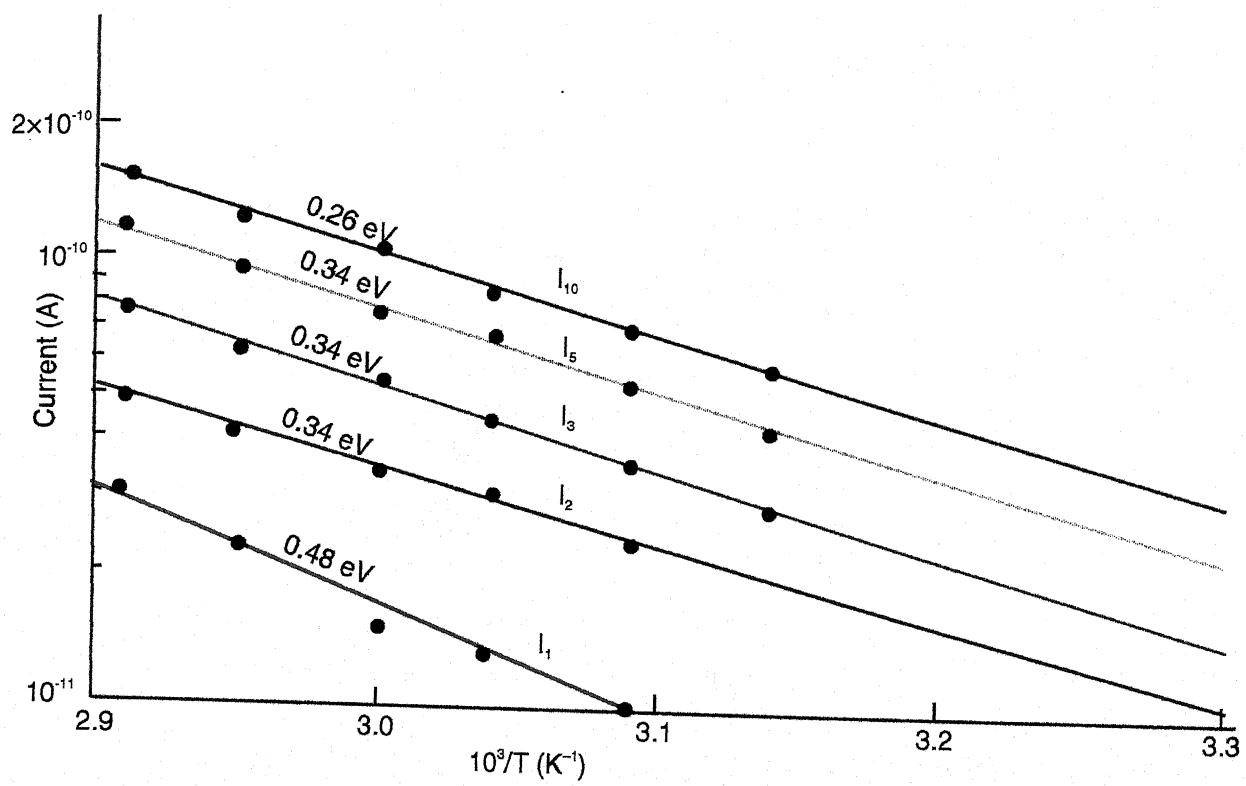
Fig. 6.4 Effect of polarizing potential on I, samples poled at 95°C for 15 minutes. The inset -1 shows peak current and charge released Vs poling potential the inset-2 shows activation energy Vs polarizing voltage.
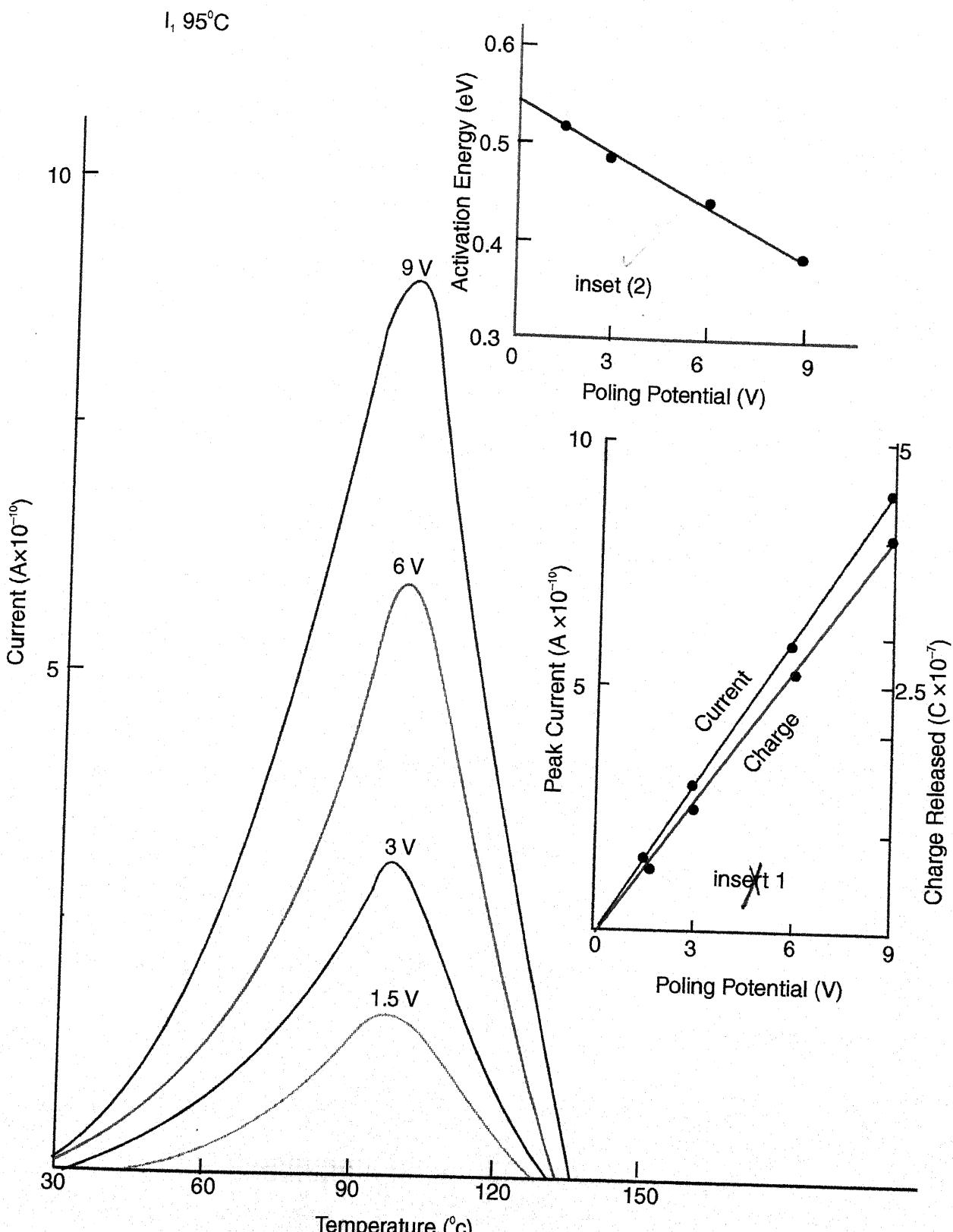
The parameters H and τ_0 may be determined from a straight line plot of the remaining charge divided by the current at a particular temperature versus the inverse of that temperature. This method is referred as the modified Bucci (or BFG) Plot.

6.3 Result:-s

Unpoled PS films give no TSC. Iodine doped films were found to give TSC. The films were never polarized. TSC spectra of I_1, I_2, I_3, I_5 and I_{10} are shown in fig. 6.1. Peak current Vs iodine concentration has been plotted in fig. 6.2 The plot is linear upto about I_5 and then shows a strong saturation.

Initial rise plots of TSC spectra of fig. 6.1 are shown in fig. 6.3. The activation energy is noted on the plot. It may be said that the activation energy decreases with the increase in concentration.

The effect of polarizing voltage on I_1 samples is shown in fig. 6.4. The voltage applied are 1.5, 3, 6 and 9 volts. Peak current and charge released increases with the voltage (insert -1) while activation energy decreases (inssert -2). Nearly same type of results were obtained with the other samples like I_2 and I_3.

Fig. 6.5 TSC Spectra of PS and I_1, I_5 and I_{10} samples under the identical thermoelectric history
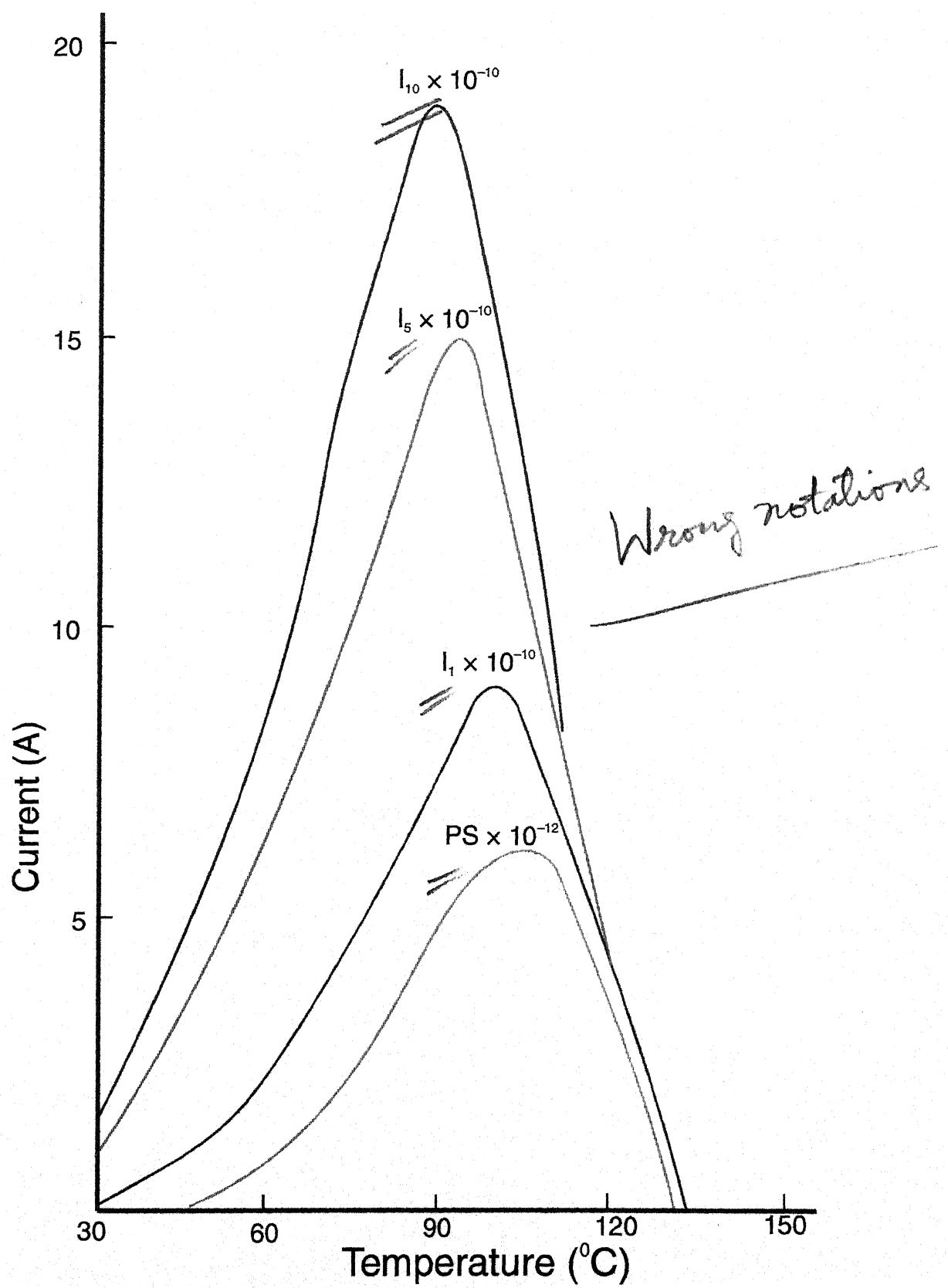
Fig. 6.6 Initial rise plots of TSC spectra of fig 6... the insert shows activation energy Vs. iodine concen...
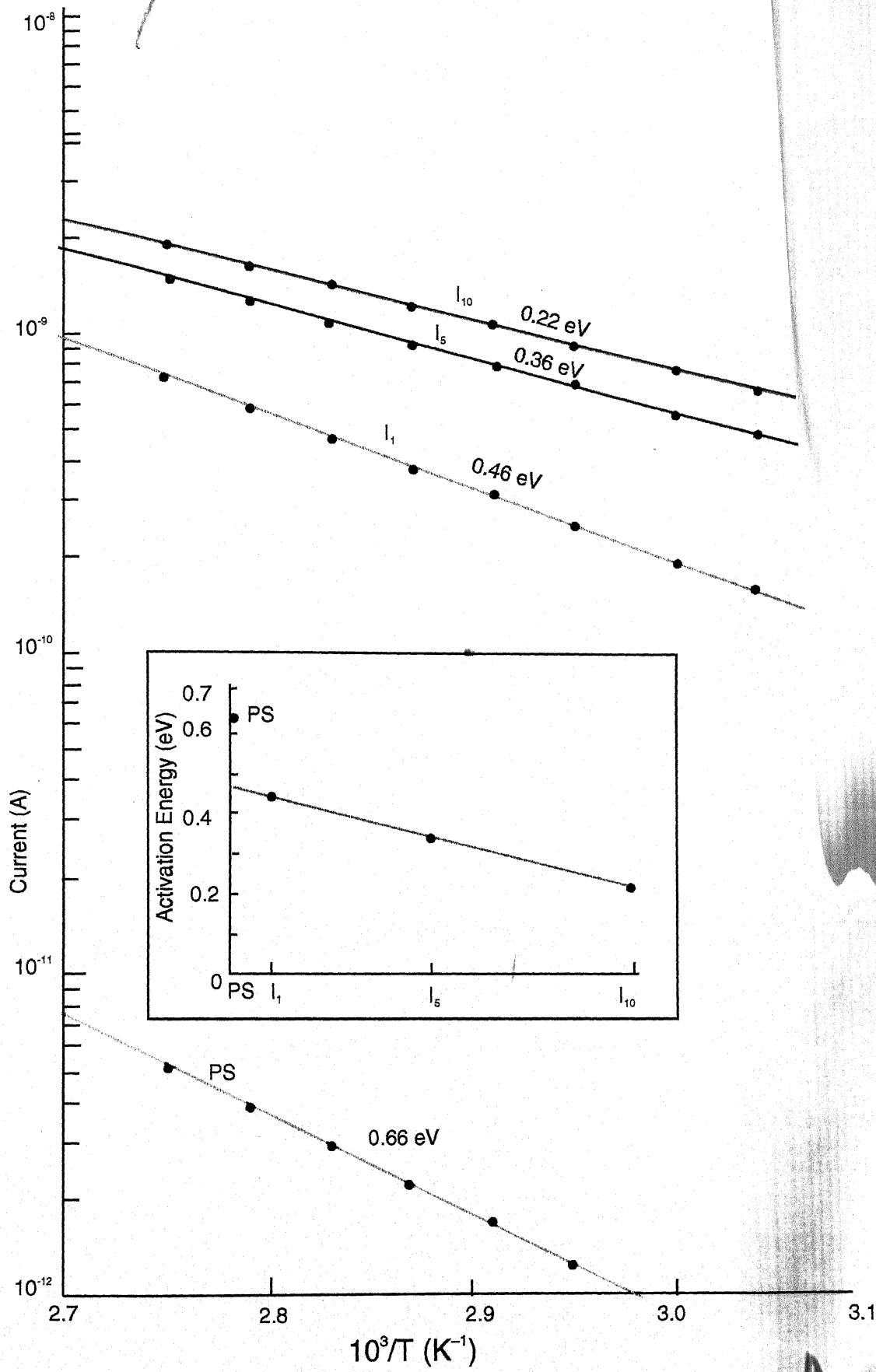
Fig. 6.7 Electrode effect on I_1 samples ploted at 95°C for 15 minutes
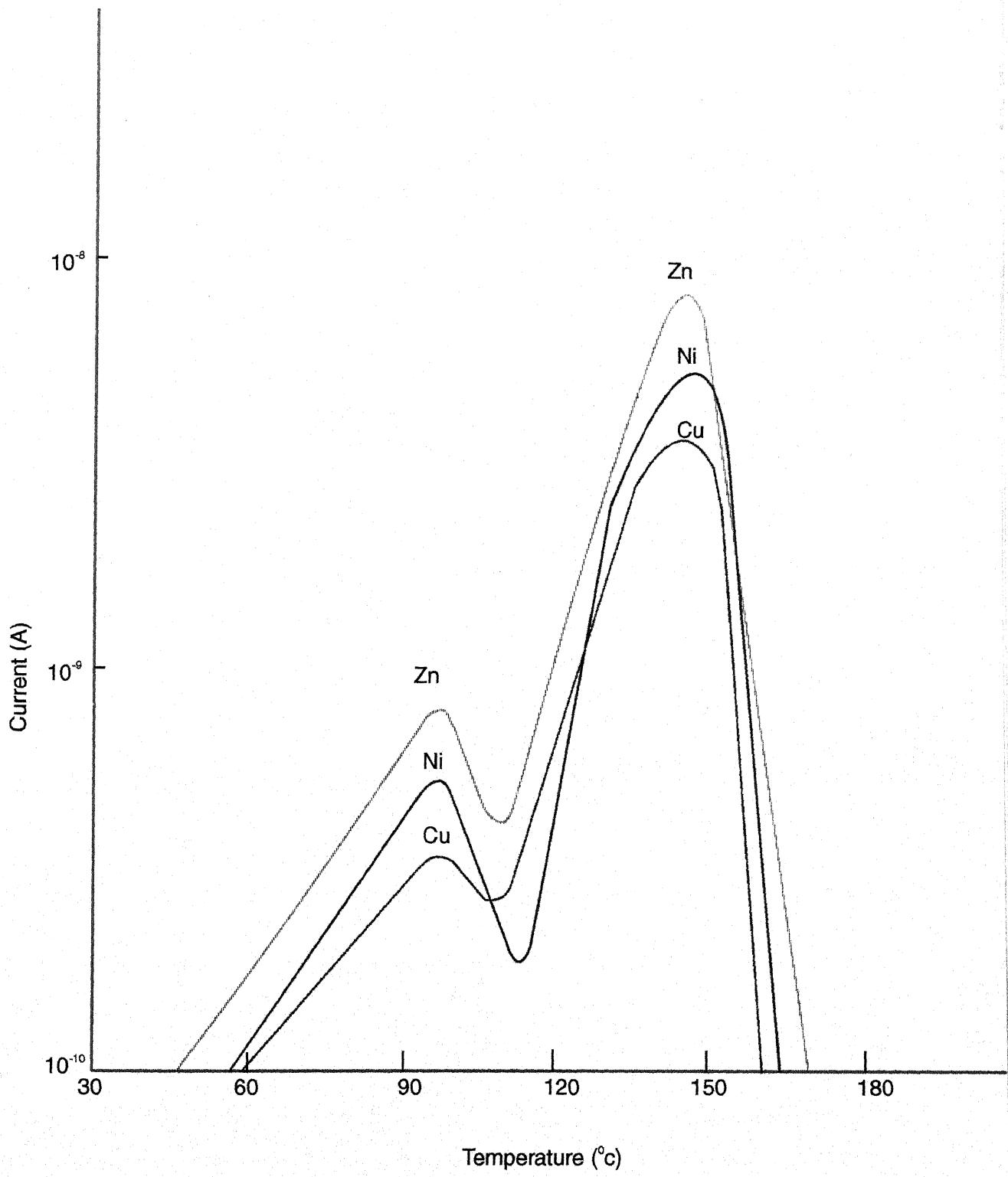
Fig. 6.8 Initial rise plot for low temperature peak of TSC spectra of fig 6.5
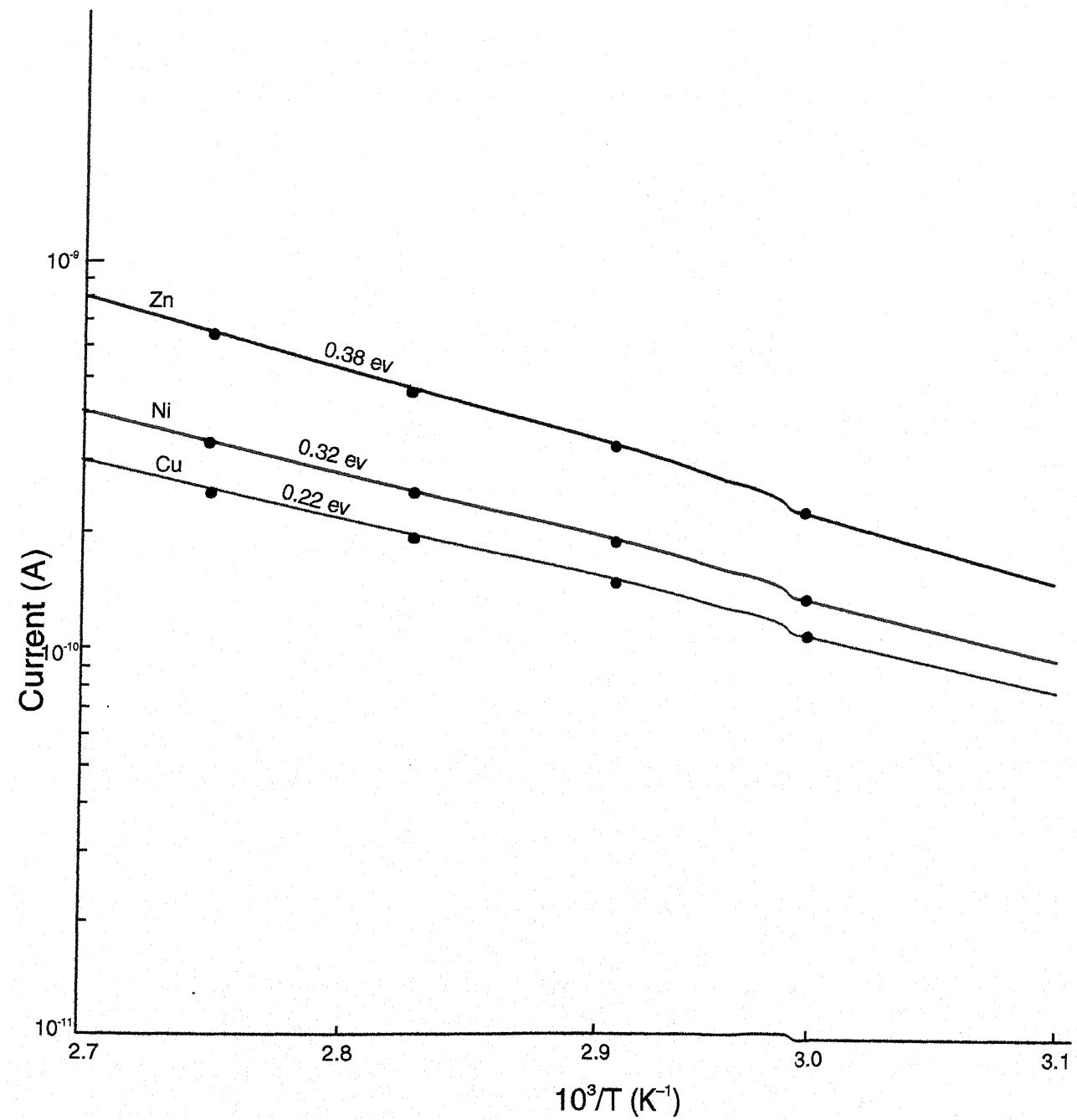
Fig. 6.8 Initial rise plot for low temperature peak of TSC spectra of fig 6.5
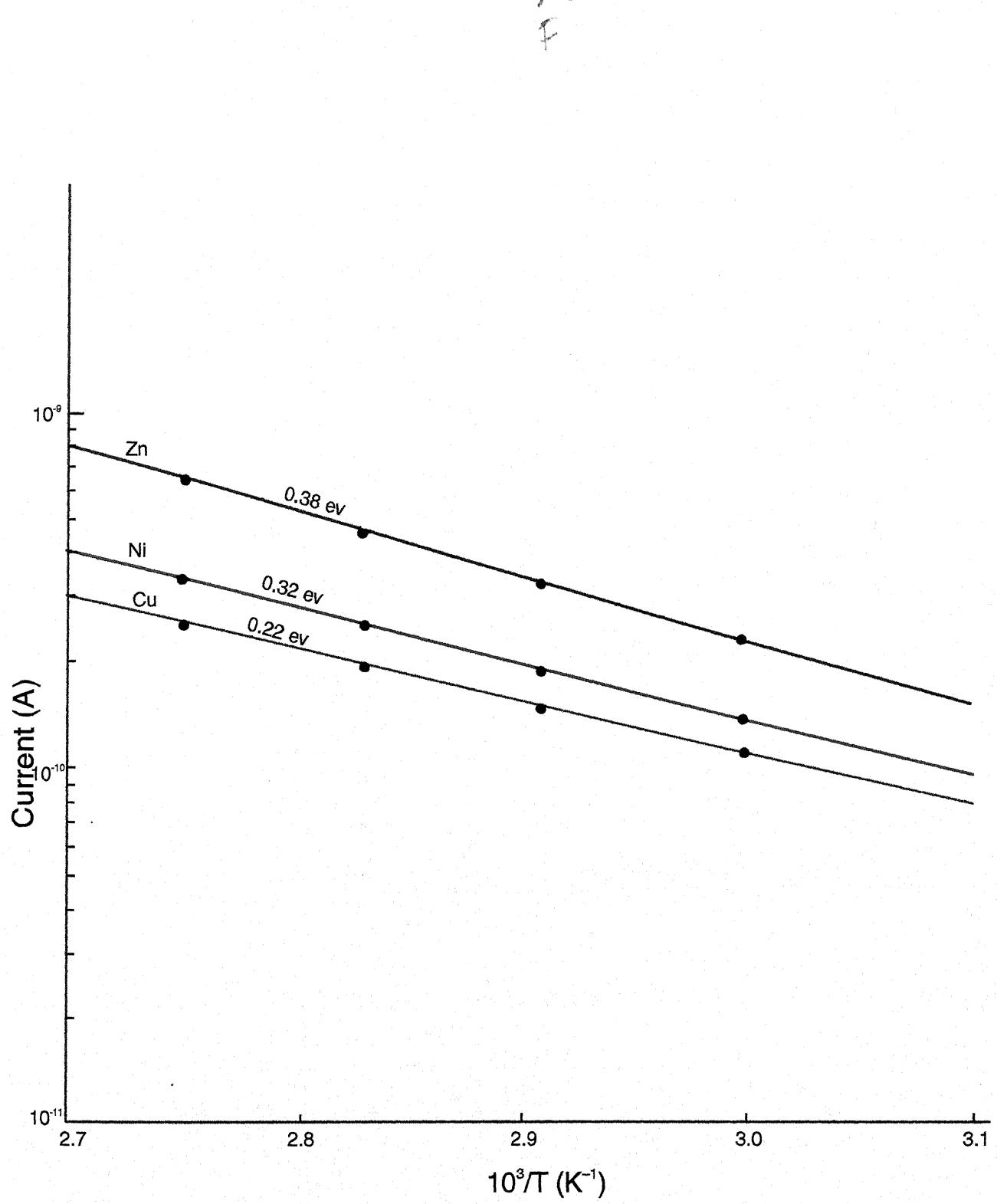
Fig. 6.9 Initial rise plots for high temperature peak of TSC spectra of fig 6.5
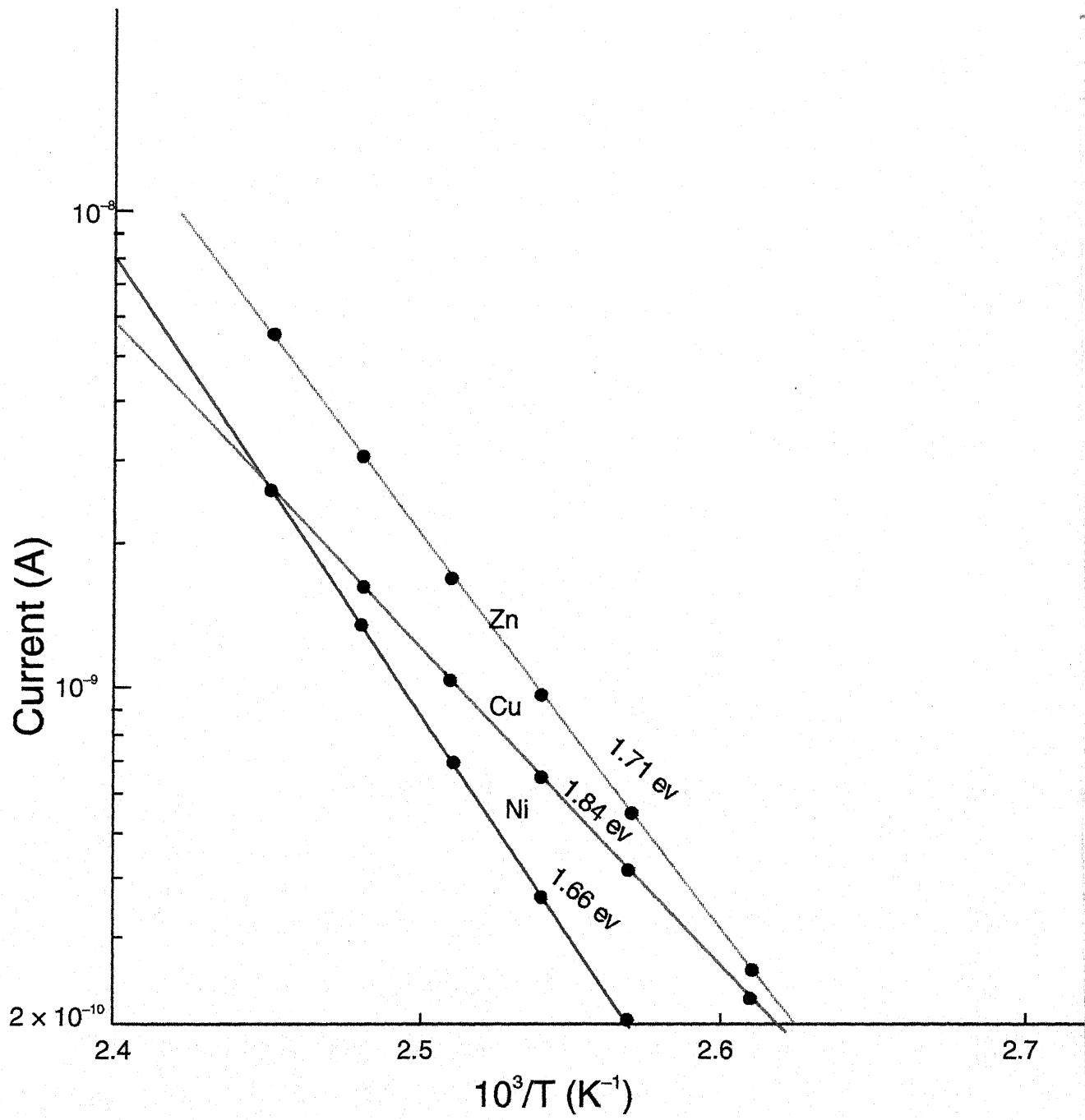
Fig. 6.5 compares TSC spectra of PS, I_1, I_5 and I_{10} under the indentical thermo electric history. Current for PS is of 10^{-12} order. For I_1 it is hundred times greater than PS. Increase in concentration of iodine has less effect (I_5 and I_{10}).

It may be mentioned that small quantity of iodine enhances the current hundred times. Initial rise plots of TSC spectra of fig 6.5 are shown in fig. 6.6. Activation energy is noted on the plot. Incorporation of iodine has an effect of shifting the TSC peak of PS from $105^0 C$ to $100^0 C$. Due to increase in concentration shifting is less. Due to doping activation energy is decreased. This is shown in the insert of fig 6.6.

Fig. 6.7 shows the effect of electrode material Cu, Ni and Zn on TSC spectra of I_1 under the identicaat condition of polarization. All the spectra consefts of two peaks. How temperature peak is α-peak and high temperature peak is ρ-peak. Initial rise plots of these peaks are shown in fig. 6.8 and 6.9 respectively. Activation energy is noted on the plots. For α-peak it seems that the activation energy decreases with the increase inmetal work function. It is not observed so for ρ-peak.

6.4 Discussion

Application of an electric field always produces a small movement of charges within the atoms of a dielectric, displacing the negative electronic cloud relative to the positive nucleus and thus temporarily generating a small dipole moment and a consequent atomic or defromation polarization. This effect occures within very short-time. Its time scale can not be changed from outside. Thus its influence on the persistent polariztion of the electret can be disregarded. Many dielectrics, including polymers, contain molecules that have an electric moment. An applied field tends to align these elementary dipoles along its own direction and thus produces an electric moment of the whole body giving rise to dipole polarization, essentiallyl a volume effect.

All dielectrics contain a small number of free charge carriers, ions or electrons or both. An electric field tends to separate positive from negative charges and to move them toward the electrode. The structure of many polymers is not homogeneous, there exist microscopic domains or grains separated by highly resistive interfaces. In this case the charge carriers can move relatively freely only with single grains, piling

up along the barriers which they are unable to surmount as they lack the necessary energy. Alternatively, when the dielectric contains many irregularly distributed traps with widely different well depths, carriers might move in the direction of the field until they fall in to deep traps from which they do not have enough energy to escape unless reactivated by a temperatue increase. Both these interfacial polarization effects constitute again a volume polarization.

Ionic conduction currents in homogeneous dielectrics usually lead to the formation of space charge clouds in the electrode regions. The effect results in a macroscopic space charge polarization of the dielectric.

The sources of the internal polarization described so far have been charges originating from and remaining within the dielectrics, but a polarization can also be caused by the deposition or injection of charge carriers from outside. Deposition of equal and opposite charges on opposing surfaces of a dielectric produces an external polarization. The distinction between internal and external polarization is due to Mikola (26). Charges can also be shot into the dielectric using penetrating electron beams. Such

electron charged dielecterics now are also called electrets, a rather loose use of the term.

The degree of polarization and its rate of decay depend on the nature of the dielectric and the experimental conditions, in particular the temperature. A dielectric becomes an electret when the rate of decay can be slowed down so much that a significant fraction of the field induced polarization is preserved long after the polarizing field has been removed.

Dipole orientation is strongly temperature dependent; at high temperature the forces opposing rotation are lessened. Thus a high degree of polarization can be achieved in a short time by application of an electric field at a high temperature. If the dielectric is cooled and the field removed only after a low temperature has again been reached, dipoles return to the original disordered state vary slowly because rotaion is hindered by strong viscous forces. The polarization is thus frozen-in. A similar behaviour is found in the case of space-charge and interfacial polarization.

The mobility of charge carriers is very low at room temperature, but increases strongly with temperature. Thus the

previous reasoning applies here too. Space charge clouds and charges accumulated along interfaces can be frozen-in.

All types of internal polarization lead to surface charges which have the oppsite polarity to that of the corresponding polarizing electrodes. Therefore heterocharge formation should be and is, a very general effect. Every decrease of the internal polarization due to rotationi of dipoles or recombinations of ions within the dielectric frees image charges which flow back through the external circuit where a discharge current is recorded. Analogously every increase of polarization gives a charging current. Therefore, build up and dissipation of internal polariztion can be investigated by means of current measurement. Current peaks are observed at temperatures where dipole orientation or carrier release from traps is activated.

The processes taking place during discharge are similar to those occurring during charging. (Generally speaking, they only behave in a opposite way). The net charge of an electret usually arises from aligned dipoles and space charge. The later are excess charges which cause the electret to be not locally neutral. However, before the electret formation the neutral polymer

already contained free charges, they manifest themselves in a conduction current, when a field is applied. So in addition to the excess charges there are free equilibrium charges in the electret. These do not contribute to its ohmic conductivity. In heteroelectrets the excess charges are intrinsic and bipolar. They originate from those charges that first take part in conduction and were accumulated near the electrode during formation. This field motion is opposed by diffusion. Moreover, during their transport a part of the charges is lost by recombination with opposite carriers.

The decay of the charge of an electret during TSC results from dipole reorientation, excess charge motion and ohmic condition. The first process will be clear, the thermal agitation will reorient the aligned dipoles at random. The motion of excess charges originates from space charge limited drift and diffusion. The first motion is due to the local electric fields forcing the mobilized excess charges to drift towards opposite charges, where by electric neutrality is restored. The excess charges will eventually recombine either with their oppose image charges or with opposite excess charges with in the polymer. Whichever, is the case, their gross motion should generate a discharge current

opposed to the charging current (58).

The temperatue dependence of the dipole reorientation can be differed from the motion of excess charges. The later will confirms closely to that of ohmic conduction from which the charges often originate. In paticular, we may expect the current maxima for dipole reorientation to occur at lower temperature than that of the excess charge motion. The first process requires only a rotational motion of molecular groups, whereas the later process involves a motion of molecular groups (ions) over macroscopic distances. The activation energy predicted theoretically by Raddish (604) for the relaxation process resulting from the local twisting of the main chain or the orientation of the side groups in a polymer is about 0.2eV.

Polyblends which are mixture of two homopolymer are charcterized by two peaks (605-606). In co-polymer well difined complex and partial phase segregation depending on molecular mass are observed (607). Saraf et al (608) have dicussed the effect of heationg rate, polarizing temperature and eletrode material on TSC specra (608). A study of charge storage and relaxation process in polymide flurocarbon polymer has been

done. In electron beam irradiated polymer films the depth increases with increasing injected charge density (609). Origin of high temperatue peak in polymide films has been attributed to the space charge (610). The relationship between activation energy and pre-exponential factor of the relaxation time has been discussed (611).

Only one TSC peak at 105^0C is observed for pure PS film, It is near glass-transition temperature of PS. Wada et al (172) obsered a temperature- transition at 110^0C in the main relaxation region of PS in dilatometric and accoustic measurement. So the peak may be identified as the α-peak intimately connected with the molecular chain-motion of the polymer. The value of the activation energy also supports this view. The α-peak is shifted to 100^0C due to doping of PS with iodine. It may be argued that iodine facilitates the segmental motion of the main chain of PS.

6.4 (a) Unpoled TSC

Iodine doped PS films gie unpoled TSC. It is due to formation of charge transfer complexes (CTC). As the concentration of iodine is increased more CTC are formed. CTC

formation may have low activation energy.

6.4 (b) Polarizing voltage:

Dipole re-orientation and charge dettraping mechanisms are generally invoked to explain the occurrence of a TSC spectrum. TSc spectra are generally interpreted interms of dipole re-orienatation or in terms of release of a space charge. Peak position data for varing polrizing voltage (612) allow one to decide in particular whether a peak is due to dipolar process or due to release of a space charg in. Dipolar peaks increase linearly with field. Space charge peaks increase non linearly with field. However the deviations form linearity will not be very large. Linear plot for peak current versus polarizing voltage for α–peak show that in addition to dipole, this peak arises due to displacement of charges through microscopic distances. Gerson and Rohbough (30) have suggested that in some dielectics, charges suffer microscopic displacement during polarization and are trapped. On heating these charges are released and recaptured. The value of activation energy is close to the values expected on the basis of ionic trap.

6.4 (C) Iodine Concentration:-

Increase in iodine concentration has an effect of enhancing the peak currrent. Iodine is dipolar and semiconductive. With the increase in dopant concentration conductivity of the film is increased. Hence more space charge is accumulated during formation. Moreover, the doped film may possess more structural defects i.e. more trapping sites. The build up of polarization may be uniform with the dopant concentration. The decrease in activation energy due to increase in iodine concentration may be associated with the increase in carrier mobility.

6.4 (d) Electrode Effect.

Variation in electrode forming material exhibts changes in TSC spectra of iodine doped PS films. The position of peak remains unaltered due to change in electrode material but the peak current is changed. For the metal of higher work function, peak current and activation energy is smaller. The ρ-peak occurs at different temperature for different metal contact. Peak current and activation energy are also changed. The values are lower for a metal of higher work function. Dipolar peaks remain unifluenced by the choise of electrode material (58).

Therefore, the origin of α-peak is not purely dipolar. Ionic polarization is also responsible for this peak. The interpretation of ρ-peak appears to be reasonably possible in terms of charge detrapping of a space charge built-up due to carriers injected from the electrodes into the film and are then trapped. It is only at temperatures above the glass transition of PS that the molecular chains are sufficiently agitated to release the charges. The amount and the sign of charge injected depend on the relative work function of the metal polymer interface. The various metal polymer interfaces possess different charge exchange rates which change the space charge storage and the current released by diffusion. The first stage of charging is carrier injection and the second stage is the entrapment of these charges in the border layer.

6.5   Conclusions:-

TSDC of iodine doped PS films has been investigated as a function of polarizing voltage, iodine concentration, and electrode material. The study enables to draw the following conclusions.

1. Iodine facilitates the segmental motion of main chain of the

polymer shifting α-relaxation of PS to a lower temperature.

2. Addition of iodine in the polymer enhances greatly the intesity of α–peak.

3. Dipolar and ionic polarization are responsible for α–relaxation peak.

4. Space charge polarizatin is responsible for ρ–peak

5. More and more space charge is accumulated due to increase in iodine concentration.

6. Mobility of charge carri0ers is increased due to increase in iodine concentration.

7. Electrode variation reveals that charge carrier injection decreases with the increase in metal work function.

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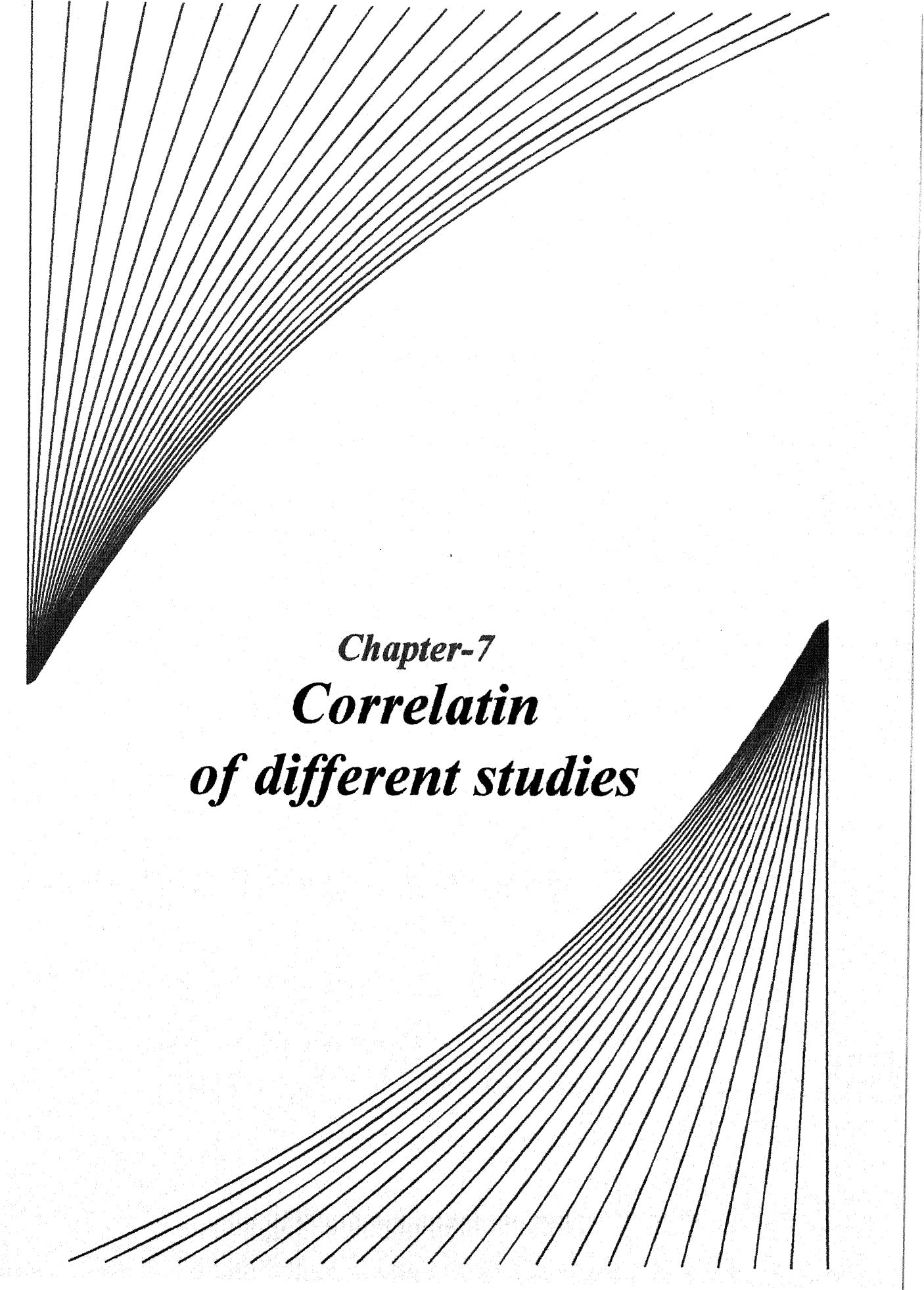
Chapter-7
Correlatin
of different studies

CORRELATION OF DIFFERENT STUDIES

It is well known that many dielectrics including polymer such as PS, show a polarization which is out of phase with polarizing field. This leads to electrets in the case of a persistent or semipersistent polarization or to the dielectric absorption, manifestations of which are short circuit currents or open circuit voltages. Many physically different mechanisms may be responsible for these effects. Among them are interfacial polarization, ionic polarization due to migration of ionic carriers over macroscopic distance, movement of space charges perhaps due to carrier injection from electrodes or other inhomogeneities and dipole orientation effects.

Dielectric loss measurement of PS film shows a peak round 85⁰C. TSC spectra of PS exhibits peak round 105⁰C. These are well near the glass-transition temperatue of PS. Due to doping of PS with iodine, loss maxima as well as TSC peak is shifted to a lower temperature. The activation energy of relaxation process is increased. Iodine incorporation in PS enhances its conductivity. Photo depolarization current is also increased due to maxing of iodine in macro molecular substnace.

Dielectric loss maxima may be attributed to the motion of phenyl group. However, it is not possible in TSC because of the relatively high temperature (20-40^{0}C) upto which the electrets were cooled during the formation. At these temperatures, the local motion sof the pheynly group remain mobilized and are not frozen- in during the cooling phase of electret formation. On the other hand, TSC peak lies in the main relaxation region of the polymer. Its origin can not be assigned to dipole reorientation only because of the fact that PS is a nonpolar polymer and moreover, the dipolar contribution calculated from Deby's equation does not correspond to the released charge. It may be partly due to the detrapping of charge carriers. Thermoluminescence experiments are also interpreted in terms of electron detrapping. Phenyl group proides a deep trap site and enhances electret stability. New traps are created due to mixing of iodine in the matrix.

Charge storage in doped matrices can take place on three structural levels.

Primary level- The traps are on the molecular chains themselves and the charge is stored at atomic sites.

Scondary level-Electrons can become caged within groups of atoms in neighbouring molecules and are held there due to the charge affinity of these groups.

For the release the charge at a primary level, individual atomic motions are necessary while at the secondary level it is indeoendent of the motion of groups of atoms.

Tertiary Level- Charge may be stored in both crystalline and amorphous regions of the matrix or at the boundaries. Charge released in this case depends on main chain motion.

Charge stability at the primary level i.e. along the molecular. chain is determined by both the electro negativity of the ions and symmetry along the chains. Charge stability at the secondary level is better, higher the packing density and lower the branching. At high temperatures, the trapping site itself may be destroyed due to increased molecular motions.

In high insulating polymer like PS, intrinsic carrier generation resulting from Boltzmann's factor is negligible at temperatures below polymer decomposition. Marked dependence of current on elecrode material, linear dependence of charge

stored on applied field and the superlinearity of steady-state current-voltage characteristics suggest carrier injection from electrode. Charge transfer from metal depends on electron levels in which the carriers shift freely under the influence of field. Polarization and depolarization of doped films in the presence of UV Radiation indicate that incident photon eject carriers from electrodes which are injected into the film. Correspondingly, effect of electrode variation was studied in TSD, photo depolariztion and current voltage measurements. The decrease in current due to increase in metal work function implies that electron injection decreases with increaseing metal work function. The thickness of the charged layer at the electrodes which arises as a result of injected carriers depends on the potential difference and on the density of traps. It is of the order of about $500A^0$, a relatively high value which is of consequence in the anlaysis of electrical properties of films. The process of charge injection also depends on time, therefore, surface states are taken into account which can take up charge directly from the metal surface. From the surface state the injected carrier diffuses under its own field or under the external field into the bulk of the film where it is again trapped in the volume traps. Electrical conductivity

study suggests a uniform distribution of traps. The trapping sites exert a strong influence on the current flow i.e. the concentration of free carriers and their mobility. Mobility values in polymer are very low suggesting strong trapping. Increase in conductivity due to incorporation of iodine may be due to increase in mobility. Dependence of mobility on temperature points to a hopping process. Hopping is connected with charge jumps brought about by motions of chain elements and the process is related to the so called chain hopping mechanism, In the present investigation chain-hopping and trap-hopping mechanism may be invoked.

Photo depolarization experiments of films suggest that carrier generation occurs via excitions. The electrons are deeply trapped and the dissipation of polarization is bimolecular in nature.

The charge storage capability of a polymer electret and the different mechanisms contributing to storage of the charge are greatly influenced by the structure of the forming polymeric matrix. The effect in polymers can be produced not only by the conventional procedures but can also be obtained by making some structural changes by doping of the matrix with

(sutable) impurities like iodine . All the four studies of doped films reveal that the electret forming characteristics of PS can be greatly modified by doping it with iodine even in very small quantity. Doping facilitates molecular chain motion as is apparent from the shift to lower temperature of TSC and dielectric loss maxima. The conductivity and dielectric loss are enhanced due to doping, resulting in marked space charge peaks which have been observed in TSC. The foreign molecules i.e. guest molecules are undoubtedly responsible for the presence of deeper traps. The trapping activity of guest molecules depends on their electron affinities and ionisation potentials. The shallow traps are those from which carriers are released thermally and deep trapping levels occur where charge carriers stay longer.

The effect of doping may also be described in term of charge transfer complex formation . Charge complex is an aggregate in which bond formation between two molecules occurs. In terms of donor-acceptor levels, in the absence of radiation, the donation of an electron causes n-type conduction. In the same material, however, irradiation may create a pair of carriers at the level of the valence band due to high energy an electron can be transferred to the conduction band and trapped in trapping sites,

thus leading to a p-type conduction. Acceptor levels should be considered as a hole in the valence band which may result from electron trapping, leading to p-type conduction. In the same material, radiation induced conduction is n-type if a hole is trapped from the pair of created carriers and the electron is transferred to the conduction band.

* * * * * *

Summary and Conclusion

SUMMARY AND CONCLUSION

PS and iodine were dissolved in cyclohexanone. Iodine in different concentration was mixed with PS. Films of 20 μm thickness were grown on Al substrate by isothermal immersion technique. In this method of film preparation, no degradation of polymer chains take place. To investigate the electrode effect, films were also grown on Zn, Ni and Cu substrates. The substrate acted as an electrode and the other of Al of 1cm² was pressed on to the film in a laid-on electrode assembly. Four different studies of electrical conduction, dielectric relaxation, photo depolarization current and thermally stimulated discharge current were performed by employing the doped films.

Electrical conductivity was investigated by noting the transient behaviour of current and studying the effects of electrode material, film tickness and iodine concentration on the current-voltage characteristics at a constant temperature. Conductivity was also determined by measuring the current when the film was heated at a constant rate of 1⁰C per minute and applying a fixed voltage. Absorption current has been explained

on the basis of trap filling mechanism. Electrode dependence of current voltage invokes charge carrier injection from electrodes. Charge transport suggests hopping mechanism. Space charge limited conduction is found to be operative. Increase in conductivity due to iodine loading is attributed to the enhancement in carrier mobility.

Dielectric properties were investigated by measureing the capacitance and loss tangent as a function of temperature, frequency and iodine concentration. No change in capacitance with frequency suggests that polarization settles in very short time. Increase in capacitance with temperature is assigned to ionic polarization. Incorporation of increased concentration of iodine increases formation of charge transfer complexes. Dielectric loss maxima is connected to the motion of molecular chains.

Photo depolarization current was investigated by varying the polarizig time, polarizing voltage iodine concentration and electrode material. The current decay mode is found to be hyprbolic rather than exponential. Electrode effect supports charge injection from electrodes.

Thermally stimulated discharge current study was conducted by varying the polarizing voltage iodine concentration and electrode material. Presence of iodine in the polymer facilitates polymer chain motion and enables the electret to store more charge. Space charge polarization is enhanced due to doping. Charges are injected from electrodes.

In short it may be argued that electret forming characterstics of polystyrene can be greatly improved by doping it with iodine. Charge transport in molecularly dispersed systems can be visualized as transition of an electron from a neutral molecule to the neighbouring " molecularcation" (hole transport) or from the "molecular anion" to a neighbouring neutral molecule (electron transport). The term "Molecular ion" is used quite freely in this context. It includes the situation where the charge is bound rather loosely on the transport molecule and spreads substantially over neighbouring matrix molecules.

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